HUMIC ACID-BASED SUPERPLASTICIZER FOR SUSTAINABLE CONCRETE

A THESIS
SUBMITTED TO THE DEPARTMENT OF SUSTAINABLE URBAN
INFRASTRUCTURE ENGINEERING
AND THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF ABDULLAH GUL UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

By
Sümeyye ÖZUZUN
December, 2019

Sümeyye HUMIC ACID-BASED SUPERPLASTICIZER AGU
Özuzun FOR SUSTAINABLE CONCRETE 2019

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ACCEPTANCE AND APPROVAL

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APPROVAL:

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Graduate School Dean

Prof. İrfan ALAN

ABSTRACT

HUMIC ACID BASED SUPERPLASTICIZER FOR SUSTAINABLE CONCRETE

Sümeyye ÖZUZUN

MSc. in Sustainable Urban Infrastructure

Supervisor: Assoc. Prof.Dr. Burak UZAL

December, 2019

Superplasticizers are polymeric agents that improve the workability of fresh concrete and improve the mechanical properties of hardened concrete by reducing the required amount of water in the mixtures. Commonly used superplasticizers are not regarded as eco-efficient products due to their high energy consumption and high cost of raw material used in the production. There are studies in the literature on the use of humic acid as a dispersant, acting as a superplasticizer and created an intermolecular separating force by electrostatic repulsion and steric hindrance. However, the published literature is lack of studies on the use of humic acid as a superplasticizer in cementitious systems.

The aim of this study is to investigate the plasticizing efficiency of a commercially available humic acid (HA) based solution, which is actually obtained from leonardite for agricultural use, in cementitious systems as well its effects on hydration and mechanical properties of the systems at various dosages. HA based solution was evaluated comparatively with respect to lignin based and naphthalene-based superplasticizers. HA based solution showed a plasticizing efficiency similar to lignin and the naphthalene-based product. The results suggest that humic acid-based agents should be considered as eco-efficient superplasticizers due to the similar performance on workability, hydration kinetics and mechanical properties of cementitious systems when compared to naphthalene-based superplasticizer.

Keywords: chemical admixtures, humic acid, hydration, Portland cement, superplasticizer

ÖZET

SÜRDÜRÜLEBİLİR BETON İÇİN HÜMİK ASİT ESASLI SÜPERAKIŞKANLAŞTIRICI

Sümeyye ÖZUZUN

Sürdürülebilir Kentsel Altyapı Yüksek Lisans Programı

Tez Yöneticisi: Doç. Dr. Burak UZAL

Aralık – 2019

Süper akışkanlaştırıcılar, taze betonun işlenebilirliğini artıran ve karışımlarda gerekli su miktarını azaltarak sertleşmiş betonun mekanik özelliklerini geliştiren polimerik ajanlardır. Yaygın olarak kullanılan süper akışkanlaştırıcılar, yüksek enerji tüketimi ve üretimde kullanılan yüksek hammadde maliyeti nedeniyle eko-verimli ürünler olarak kabul edilmez. Literatürde hümik asidin dispersant olarak kullanımı, bir süper akışkanlaştırıcı olarak işlev gören elektrostatik ve sterik itme ile moleküller arası bir ayırma kuvveti oluşturduğu konusunda çalışmalar vardır. Fakat yayınlanmış literatürde, hümik asidin süper akışkanlaştırıcı olarak çimentolu sistemlerde kullanımı üzerine mevcut bir çalışma bulunmamaktadır.

Bu çalışmanın amacı, aslında tarımsal kullanım için ticari olarak temin edilmiş leonarditten elde edilen hümik asit (HA) esaslı çözeltinin çeşitli dozajlarında, çimento esaslı sistemler içinde akışkanlaştırma verimliliğini ve bunun yanı sıra hidratasyon ve mekanik özellikler üzerindeki etkilerini araştırmaktır. HA esaslı çözelti, lignin esaslı ve naftalin esaslı süper akışkanlaştırıcılar açısından karşılaştırmalı olarak değerlendirildi. HA esaslı çözelti, lignin ve naftalin esaslı ürünlerine benzer bir akışkanlaştırma etkinliği göstermiştir. Sonuçlar hümik asit esaslı ajanlar, naftalin esaslı süper akışkanlaştırıcıyla kıyaslandığında çimento esaslı sistemlerin işlenebilirlik, hidratasyon kinetiği ve mekanik özellikler üzerindeki benzer performansı nedeniyle eko-verimli süper akışkanlaştırıcılar olarak dikkate alınması gerektiğini göstermektedir.

Anahtar kelimeler: kimyasal katkılar, hümik asit, hidratasyon, Portland çimentosu, süperakışkanlaştırıcı

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To my family

Chapter 1

Introduction

Today's modern concrete technology have indicated that plasticizers (water reducers) or superplasticizers (high-range water reducers) become an integral part of almost any general or special concrete mixture. Because the desired workability and mechanical properties can be achieved with such admixtures.

Superplasticizers generally contain three different active ingredients as naphthalene formaldehyde sulfonate, melamine formaldehyde sulfonate and polycarboxylate. These each type of superplasticizers pass through intensive energy production processes and causes high CO_2 emission. Moreover, the disposal of chemical wastes after the completion of this process is expensive and dangerous.

For example, in the production of naphthalene formaldehyde sulfonate-based superplasticizer, naphthalene, sulfuric acid and formaldehyde chemicals are used as raw materials and the raw material is obtained by first mixing at high temperature and then cooling. After the insoluble parts are mixed again with water, filtered and added to the solution. Finally, a certain pressure is applied to the samples and made ready for use. All of the raw materials and processes used in the production show that these admixtures not regarded as eco-efficient products[1].

In recent years, it has been observed that studies have been carried out to determine the environmental performance of chemical admixtures used in the concrete according to the relevant European standards and regulations. In 2014, with the agreement signed between the Concrete Admixture Manufacturers' Association and the European Concrete Admixture Association (EFCA) in Turkey, environmental product declarations for concrete admixtures were started to be prepared and the works were completed in September 2015 and presented to the use of the association members. According to the ISO 14025 standard, quantitative environmental data are provided for specific parameters (raw material production, energy use and efficiency; material and chemical content; emissions to air, water and soil; waste generation)[2].

The growing interest of both the European and Turkish concrete chemical admixtures in the production sector in terms of eco-efficient chemical admixtures with a certain environmental performance for sustainable structures clearly reflects the need for innovative products and technologies and scientific studies in this field.

Considering all this, scientific studies are needed to develop admixture that can be used as a raw material of local natural resources as an alternative to the commonly used superplasticizers and which can be obtained with easier and more energy efficient production processes.

Leonardite is a natural formation with high organic content in humic acid form formed by air oxidation of lignite around lignite deposits. The use of humic acid extracted from leonardite by alkali leaching as a dispersant in various systems is available in the literature and it is stated that this effect is caused by electrostatic forces and steric effect[3-5]. While this natural material has been shown to function as a superplasticizer and to form an intermolecular separation force, there is no study on its performance in cementitious systems.

The objective of this project is to observe the plasticizing efficiency in cementitious systems using a humic acid-based solution (HA), which is obtained from leonardite with alkali leaching method and used in agriculture. One of the main ideas of the study, humic acid-based solution is a good alternative superplasticizer for sustainable concrete due to its easier production process with less energy.

First aim of the study to show behaviour of humic acid-based solution in cementitious systems as a superplasticizer in comparison with a lignosulphonate-based (LS) and a naphthalene-based (NA) admixture in various dosages. Second aim is to examine the compatibility of humic acid-based solution with cementitious systems containing nano silica. The hydration and mechanical properties of the afore-mentioned cementitious systems were evaluated.

Chemical composition of the dried forms of admixtures were determined by X-ray fluorescence (XRF) analysis. Hydration kinetics of cement pastes prepared with and without superplasticizers were measured by using isothermal calorimetry and, free

$Ca(OH)_2$ content of the hardened pastes were determined at 3,7 and 28 days of age by thermogravimetric analysis (TGA). In addition, the flow values of the cementitious mortars were measured to observe the plasticizing performance of HA, LS and NA based superplasticizers. The effect of superplasticizers on the setting time of cementitious pastes was also observed. Finally, the compressive strength of the cementitious mortars with and without superplasticizers was determined at 3,7 and 28 days.

Chapter 2

Literature Review

To better understand the interaction between cement and admixture, it is useful to know the properties of these two materials. General information about cement and superplasticizers is given below.

2.1. Portland Cement and Its Properties

Portland cement is a product obtained by grinding the clinker obtained by burning the raw materials of the limestone and clay mixture together with a small amount of gypsum. This product This product combines with water and gains binding properties [6, 7]. The raw materials of the clinker used in cement production are limestone and clay materials as follows.

Limestone ($CaCO_3$) decomposes into quicklime (CaO) and carbon dioxide (CO_2) when exposed to high temperatures (900˚C). It may not be possible to find limestone materials mostly pure. The amount of magnesium carbonate ($MgCO_3$) can be found in the limestone, which consists of a very large amount of $CaCO_3$. $MgCO_3$ decomposes as MgO and CO_2 under high temperature effect [6].

The clay materials consist mainly of silica and alumina. When the clay is exposed to high temperature (~600˚C), it decomposes into silica (SiO_2) and alumina (Al_2O_3). Clays may contain very small amounts of iron oxide (Fe_2O_3) and other impurities[6].

Oxides such as CaO, SiO_2, Al_2O_3 and Fe_2O_3 undergo a chemical reaction by cooking among themselves and forming clinker. Table 2.1.1 shows the main constituents of the clinker that are produced as a result of firing the raw material mixture in rotary kilns[6]

Table 2.1.1 Compounds of clinker and their abbreviations[7]

Main Components	Oxide Composition	Symbol according to cement chemistry
Dicalcium silicate	$2CaO.SiO_2$	C_2S
Tricalcium silicate	$3CaO.SiO_2$	C_3S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.\ Fe_2O_3$	C_4AF

As soon as cement is combined with water, each main component reacts with water separately (cement hydration) and the cement paste solidifies (sets) and hardens (gains strength). The main components of the cement are given below[8].

2.1.1. Tricalcium Silicate (Alite) and Dicalcium Silicate (Belite)

Alite has the formula $3CaO.SiO_2$ and belite have the formula $2CaO.SiO_2$. They are shown as C_3S and C_2S respectively in cement notation. They have a complex structure depending on temperature or impurity. Due to the difficulty in preparing a single C_3S, C_2S crystal, the crystals structure information of individual polymorphs could not be obtained clearly as a result of the researches.

In general, C_3S reacts faster than C_2S during the early stages of hydration and causes a moderate heat of hydration. This process is the main stage that affects early and final strength development. C_2S has a low heat of hydration and it gains strength after 28 days of hydration.

The products formed by hydration of C_3S, C_2S are shown below with Equation 2.1.1.1 and Equation 2.1.1.2[8];

$$2Ca_3SiO_5 + 6H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 \qquad (2.1.1.1)$$

$$2[2CaO.SiO_2] + 4H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 \qquad (2.1.1.2)$$

2.1.2. Tricalcium Aluminate (Aluminate)

Aluminate has the formula $3CaO.Al_2O_3$ and its abbreviation C_3A in cement notation. Although the average content of C_3A in the cement is about 4-11%, it is very effective in initial reactions. It reacts very quickly with water and causes undesired flash set and high hydration temperature.

When C_3A reacts with water, thermodynamically unstable hexagonal C_2AH_8 and C_4AH_{13} are formed (Equation 2.1.2.1). They soon turn into $2C_3AH_6$ in stable cubic structure (Equation 2.1.2.2). This structure can also occur when the C_3A is directly hydrated at temperatures above 80 ° C (Equation 2.1.2.3).

This process is shown below;

$$2C_3A + 21H \longrightarrow C_4AH_{13} + C_2AH_8 \qquad (2.1.2.1)$$

$$C_4AH_{13} + C_2AH_8 \longrightarrow 2C_3AH_6 + 9H \qquad (2.1.2.2)$$

$$C_3A + 6H \longrightarrow C_3AH_6 \qquad (2.1.2.3)$$

In order to control the flash set of cement, some (3-6%) gypsum (CSH_2) is added to the clinker and these two materials are ground together. The reaction of C_3A, gypsum and water are given in Equation 2.1.2.4 and Equation 2.1.2.5.

$$C_3A + C\bar{S}H_2 + 10H \longrightarrow C_4A\bar{S}H_{12} \qquad (2.1.2.4)$$

$$C_3A + 3C\bar{S}H_2 + 26H \longrightarrow C_6A\bar{S}_3H_{32} \qquad (2.1.2.5)$$

Once the hydration has started, C_3A phase reacts with the gypsum in a few minutes to form ettringite. Ettringite crystals form on the surface of the aluminates in the form of fine needles. These crystals are so thin that in the early days of hydration and they do not form a rigid structure, so the flash set does not occur[8, 9]. When the gypsum in the environment is depleted, the C_3A in the system has not yet been exhausted, the remaining C_3A reacts with ettringite and is converted back to mono sulfate then it causes durability problems in the structure (Equation 2.1.2.6) [8, 10].

$$C_6A\bar{S}_3H_{32} + 2C_3A + 4H \longrightarrow 3C_4A\bar{S}H_{12} \qquad (2.1.2.6)$$

2.1.3. Aluminoferrite Phase (Ferrite)

Aluminate has the formula $3CaO.Al_2O_3$ and the abbreviation C_3A in cement notation. It is the phase that gives the cement its natural grey colour. In the presence of gypsum, the hydration reaction of C_4AF, like C_3A, is observed to slow down. Its hydration temperature is lower than in other phases. Also, ferrite has little contribution to early and final strength of cement. Based on this information, the hydration parameters of all components are briefly summarized and are shown in Table 2.1.3.1.

Table 2.1.3.1 Property of compound of clinker[7]

Property	Relative behaviour of each compound			
	C_3S	C_2S	C_3A	C_4AF
Rate of Reaction	Medium	Slow	Fast	Fast
Heat Liberation	Medium	Small	Large	Small
Cementing value, per unit compound				
Early	Good	Poor	Good	Poor
Ultimate	Good	Good	Poor	Poor

To better visualize the hydration process, the electron microscope image (Figure 2.1.3.1) of the chemical reaction is as follows;

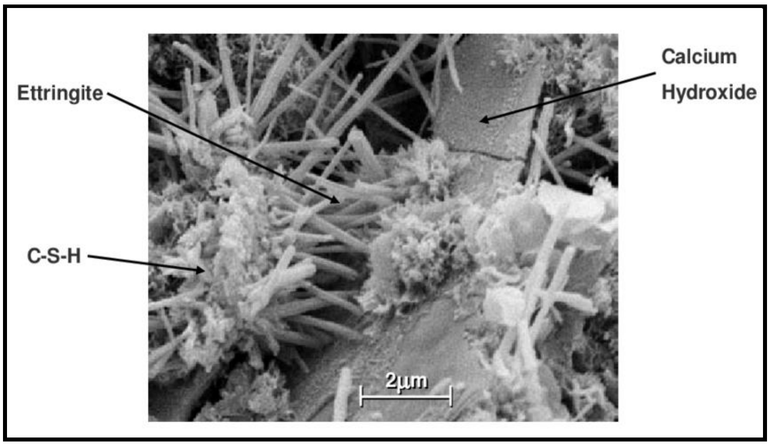


Figure 2.1.3.1 Portland cement hydration products on the electron microscope [11]

2.1.4. Hydration Kinetics of Portland Cement

Cement is a hydraulic binder and cement hydration is the irreversible exothermic reaction of cement with water. Cement contains different compounds that can react with water, and the resulting product and heat release are different as a result of the reaction of each compound[6, 7]. In Portland cement, the chemical process between the various compounds and water are described in five stages. These steps are shown in Figure 2.1.4.1 with a curve representing changes in temperature during the first hours and days of hydration [13].

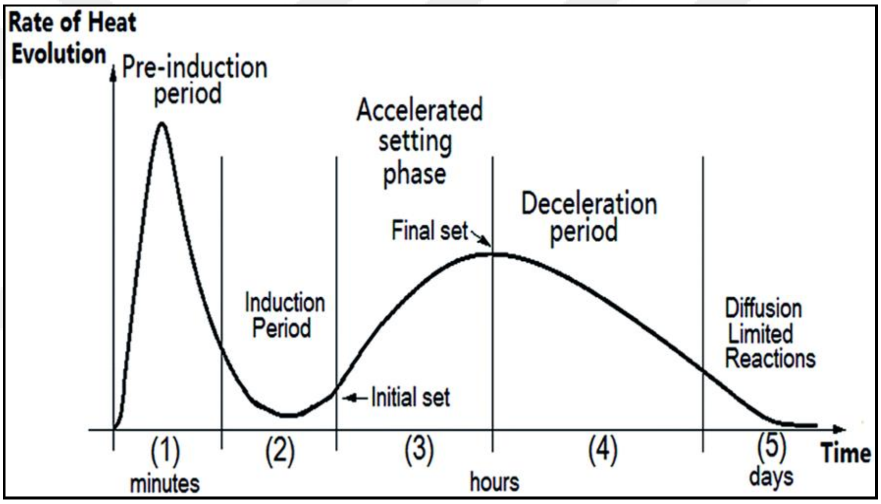


Figure 2.1.4.1 Heat evolution and process during the hydration of cement paste[12]

(1) Period of Rapid Heat Evolution: By mixing the cement and the water, the first peak is produced as a rapid heat generation which lasts for several minutes. This represents the heat of the aluminate and sulfate solutions. Because the solubility of the aluminates is descended in the presence of sulfate in solution, this first peak terminates quickly[6]. In this period the following events occur:

- Increase of various ion concentrations (Ca, K, Na, OH, Al, SO_4, …) in cementitious admixture
- The formation of fine and amorphous gel structures on the cement particle surface

- As a result of geometric formations, neighboring crystals grow by affecting each other.

(2) **(Dormant) Induction Period:** At this stage, the sulphate concentration from the gypsum acts as a predominate to form the ettringite crystals.

If the sulfate concentration is sufficient, a physico-chemical process begins:

- The growth of the ettringite crystals continues
- The production of C-S-H gels covering the aluminate-rich gel layer increase
- Development of osmotic and mechanical pressures as the hydration moves inward in the cement particle.
- Ca^+ ions and OH^- concentrations increase in solution [13].

(3) **Acceleration Period:** According to the NMR (Nuclear Magnetic Resonance) results at the end of the induction period, the hydration products formed until the end of the induction period contained only monomeric silicate, dimers and larger ions. In the acceleration phase, the reaction rate and heat evolution reach their highest values. At the end of this stage, the final set of paste is completed. This peak is caused by C-S-H and CH formed after hydration of C_3S and then the heat release is slowed [14, 15].

(4) **Period of Slowing Down:** At this stage, the rate of increase of hydration continues by slowing down. The resulting hydration products began to take up more space than clinker mineral particles. Second C_3A reaction peak may be noticed in the decreasing graph curve due to consuming gypsum[6].

(5) **Steady State Period:** Since belite (C_2S) dissolves and reacts more slowly than alite (C_3S), it begins to react at this stage and produces C-S-H and CH. After which the reaction proceeds slowly in a controlled diffusion.

In the case of Portland cement paste, the rate of hydration increase rate when the cement compounds are handled one by one and are as shown in Figure 2.1.4.2.

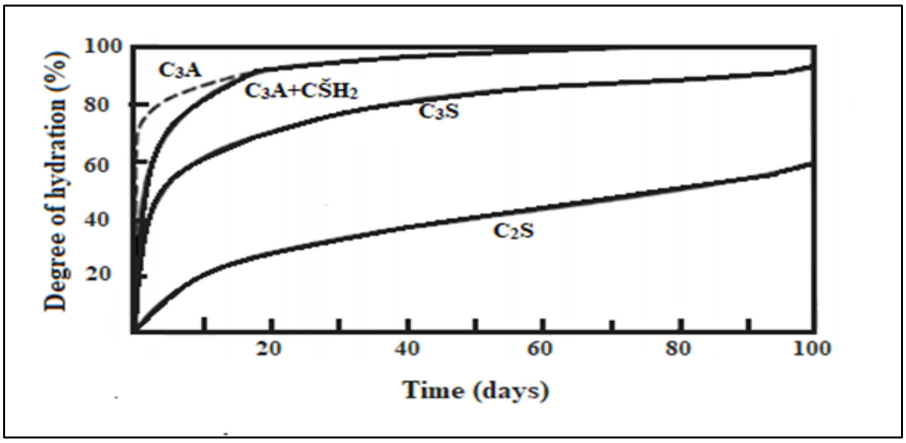


Figure 2.1.4.2 Hydration rate of each hydration compound [7]

2.2 Chemical Admixtures for Concrete

Concrete admixture is a material that is added to the concrete mixture at the same time or before and increases the usage efficiency of the concrete. Recently, with the expected performance increase from concrete, the use of admixtures in the production of concrete or mortar has become inevitable. They have become an important component in concrete as water, cement, fine sand and stone. At present, chemical admixture types in EN 934 Standard as given[16-18]:

- Normal plasticizing/water reducing (WRA)
- Super plasticizing/high range water reducing (HRWRA)
- Retarding & retarding plasticizing
- Accelerating-set and hardening types
- Air entraining
- Water retaining
- Water resisting (water proofing)
- Retarded ready-to-use mortar admixtures
- Sprayed concrete
- Grout admixtures for prestressing

2.3. Superplasticizers and Their Properties

Plasticizers also are known as natural or artificial water-soluble polymers, they are often used in the concrete industries as a dispersing agent. Looking at the current state of modern concrete technology and applications, it is observed that plasticizer or superplasticizers become an integral part of almost any general or special concrete mixture. Admixtures in the mixing water reduction ratio of 5-12% compared to control concrete are classified as water reducers or plasticizers, and more than 12% are classified as high water reducers or superplasticizers.

Superplasticizer chemicals have two basic functions on the mixture, one of which reduces the amount of water in the mixture and reduces the capillary porosity of the hardened cemented material, and the other is to maintain certain workability of the fresh concrete for a reasonable period of time. The most common superplasticizers used are divided into four classes: sulfonated melamine formaldehyde condensate, sulfonated naphthalene formaldehyde condensate, modified lignosulfonates, and polycarboxylates.

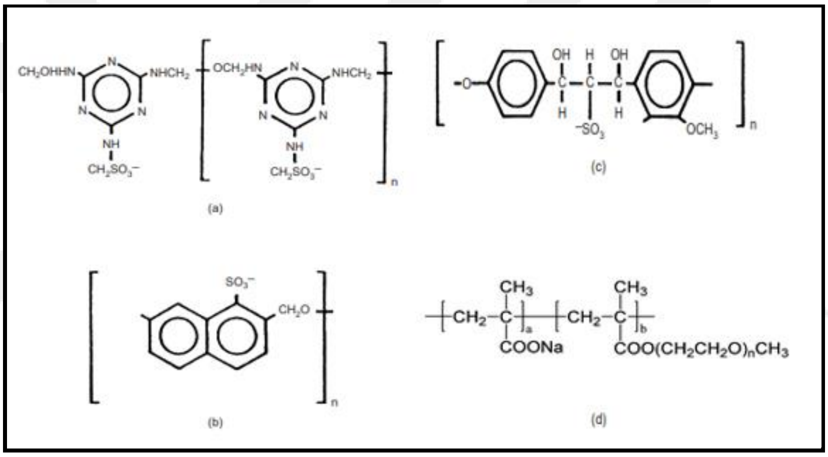


Figure 2.3.1 Structural formulae of (a) sodium salt of sulfonated melamine formaldehyde; (b) sodium salt of sulfonated naphthalene formaldehyde; (c) modified lignosulphonate; and (d) carboxylate [19]

Polynaphthalene sulfonate from the group of superplasticizers are the first and most widely accepted compounds, the molecular shape structure is shown in Figure 2.3.1(b). This illustration shows linear oligomers with sulfonate groups at position β. **S**econd sulfonate-based superplasticizer family also commonly used in the concrete industry is polymelamine sulfonates, the typical molecular structure shown in figure 2.3.1(a). Lignin is a natural macromolecular compound made of poly-phenylpropane units and containing various active functional groups including alcoholic and phenolic hydroxyls, methoxyl, carbonyls. Due to these functional groups, it provides a large number of reactive sites for other chemical reactions. The derivatives of lignin are used in many fields, and one use is as a dispersing agent and its structure shows Figure 2.3.1(c) [20]. Carboxylates have several side chains attached to a common polyacrylate or polymethacrylate main chain. Due to their carboxylic and sulfonic functional groups, polymers ionized only in alkali environments. When all the side chains on the main chain are shown aligned in parallel, this polymer appears as a vertical comb, so they are called comb-like polymers figure 2.3.1(d) [21].

2.4. Production of Superplasticizers

Superplasticizers can perform better or worse than each other even if they have the same origin. Shiping et all have stated that in order to understand the reason for this and to determine the mechanism of superplasticizers in concrete, it is necessary to know how they are produced[17, 22].

In order to gain insight into the manufacture of superplasticizers, the synthesis steps of the most commonly known naphthalene-based superplasticizer will be briefly described. These steps are called sulfonation, condensation, neutralization and filtration.

2.4.1. Sulfonation

In the first step, sulfuric acid and naphthalene are mixed in appropriate proportions in the heated reactor. The acidic sulfonate group (HSO_3) binds to the naphthalene molecule in two different positions. If it is connected at 12 o'clock, it is called “α” position and if it is connected at 2 o'clock it is called “β” position as shown in figure 2.4.1.1.

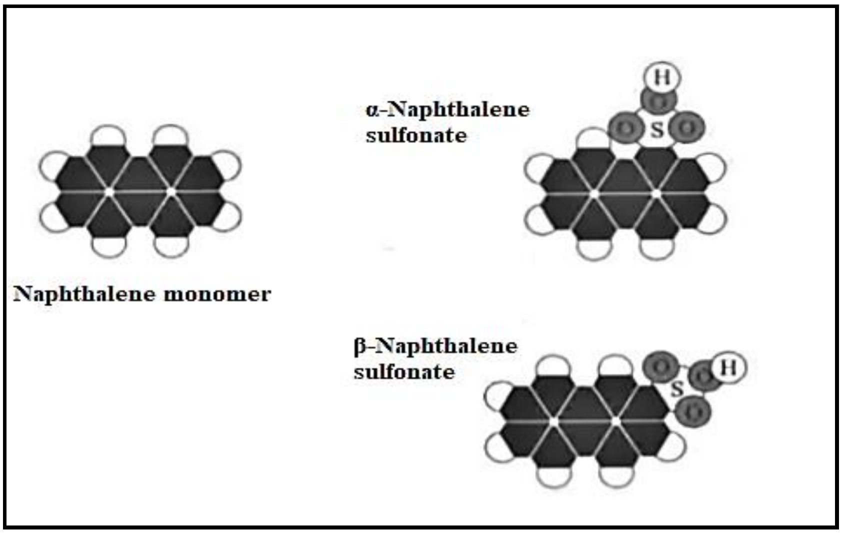


Figure 2.4.1.1 α- Naphthalene sulfonate β - Naphthalene sulfonate is illustrated in the sulfonation step in the fabrication poly naphthalene superplasticizer [21]

The coupling of the sulfonate group to the superplasticizer molecule as the β position makes it more efficient. Therefore, admixture manufacturers are required to adjust the thermodynamic parameters during production to ensure that the sulfonate group has the maximum of β positions. However, it is almost impossible for all sulfonate groups to bind in the β position. If the control during production is not good, only 50% of the total sulfonate groups are bound in the β position. If the control is good, this value can be 85-90%. The α or β position of the sulfonate group is determined by the magnetic resonance method[23].

Another important point in sulfonation is the number of sulfonated areas on the molecule. Theoretically, although each naphthalene molecule has two domains, one in each carbon ring, practically only one domain is sulfone. If the ratio of the number of sulfonated groups to the number of positions present in the polymer is about 0.90-0.95, it can be said that the sulfonation is near perfect[17, 23]. Hsu and other (2000) similarly defined the degree of sulfonation as the “sulfur/carbon” ratio; this ratio represents the number of sulfonated groups in the molecule[24].

2.4.2. Condensation (Polymerization)

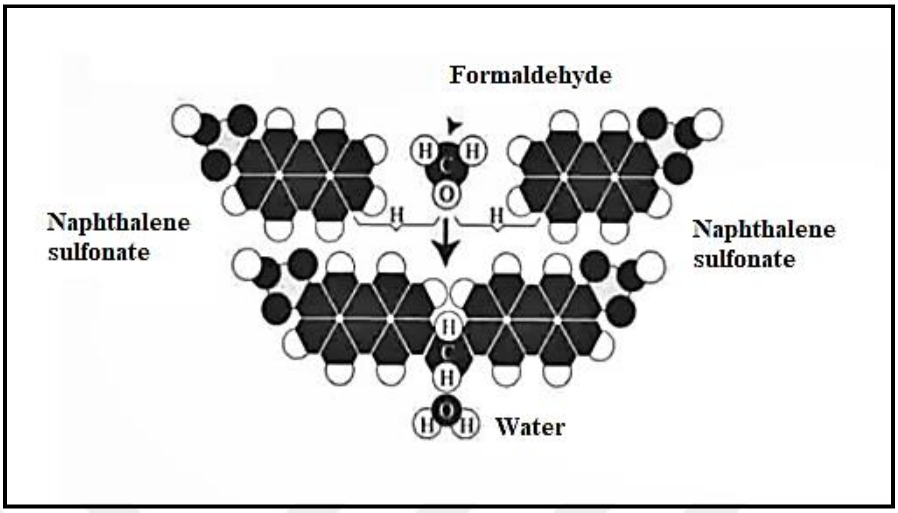


Figure 2.4.2.1 Second step of the fabrication of the polynaphthalene[22]

Polymerization of naphthalene groups takes place by condensation reaction between 2 naphthalene groups and 1 formaldehyde molecule (Figure 2.4.2.1). In order to keep the molecule chains as long as possible, manufacturers must keep the condensation conditions under control[25].

Generally lengthening the polymer chain increases the level of superplasticizers viscosity. But, branching or cross-linking of polymer chains may also increase the viscosity of superplasticizer. That is, the increased viscosity of superplasticizer is always it may not mean that the polymer chain is long and the increase in the performance of superplasticizer cannot be directly related to such a situation[25].

If the average degree of polymerization is greater than 9-10, it causes an increase in molecular weight and consequently, an increase in viscosity is observed. Since this increase is due to the increase in cross-linking rather than the linear lengthening of the polymer chains, the efficiency of superplasticizer begins to decrease. Molecular properties including molecular weight and distribution are measured by gel permeation chromatography (GPC)[25].

2.4.3. Neutralization

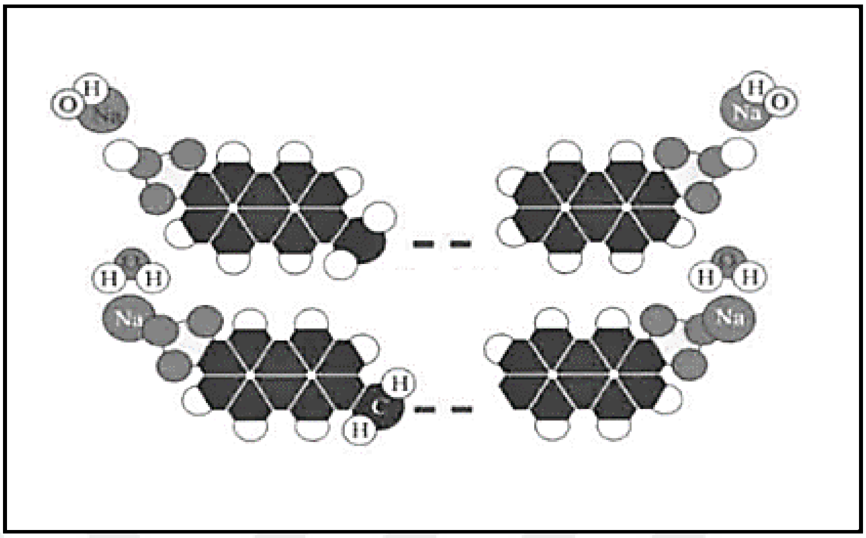


Figure 2.4.3.1 Third step of the fabrication polynaphtalene[22]

The pH of naphthalene sulfonic acid is about 2-3, which is very low for a high pH cement-water mixture. Thus, the sulfonic acid should be neutralized using a base. Although NaOH is the most commonly used base, $Ca(OH)_2$ is also sometimes used. Sodium or calcium salts are formed as a result of this process (Figure 2.4.3.1). In literature, it has been found that other cations are used to neutralize the sulfonic acid such as Li, Zn, K, Mg, Ca, NH_3 [17, 26].

2.4.4. Filtration

This is the process of removing the sulphates from the system so that the active solids (the polymerized chains) can be in as many quantities as possible in the superplasticizer molecule. Manufacturers generally specify the total solids content in their products. The ratio of active solids is rarely indicated. At the end of the production process, the obtained naphthalene superplasticizer is a dark brown liquid. The solid content of this liquid is generally between 22 and 42%[27].

As a result, important parameters affecting the performance of naphthalene-based superplasticizers can be listed as follows[17]:

- Coupling of sulphonate groups in the α or β position (better performance in the β position),
- Amount of sulfonated naphthalene groups in each naphthalene ring,
- Degree of polymerization (the optimum number of polymerizations is considered to be around 9-10 to avoid excessive branching and crosslinking in the naphthalene-based superplasticizer),
- The total amount of active solids.

2.5. Mechanism of Action of Superplasticizers

The dispersibility of cement particles in the presence of superplasticizer is generally explained by the “electrostatic” and “steric” mechanism of action. For the workability of a cementitious system, the repulsive forces must be stronger than the adhesion forces between the colloidal particles, namely Van der Waals or electrostatic forces [13].

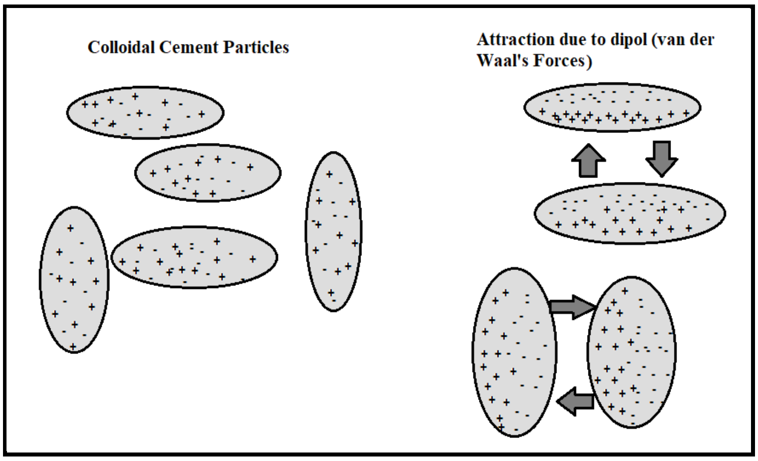


Figure 2.5.1 Van der Waals forces

Van der Waals forces cause aggregation of particles in a cementitious system (Figure 2.5.1). They are the attraction forces due to dipole-containing particles. These particles have an electron distribution at one end of the electron density that is higher than the other. The forces are active in the immediate vicinity of the particles and are of considerable importance for small particles [13].

The following is an overview of the two effects of superplasticizers.

2.5.1. Electrostatic Effect

Superplasticizers are composed of high molecular weight (20,000 to 30,000) long chain, and anionic surfactants with multiple polar groups in the hydrocarbon chain. They act by adsorption in the solid-liquid interface between the cement particles and the aqueous phase in concrete. When the polymeric dispersants are adsorbed on the surface of cement particles, the dispersants cause a strong negative charge distribution which helps to significantly reduce the surface tension of the surrounding water and greatly increase the fluidity of the system[6, 7, 28].

The dual-layer model describes the ionic environment around the charged colloidal particle and how the electrical repulsive occurs. Initially, positively charged ions adhere to the colloidal negatively charged particle charged with a high negative charge, thereby forming a layer of positive charges around the particle. This layer is called the “Stern layer “as shown in (Figure 2.5.1.1).

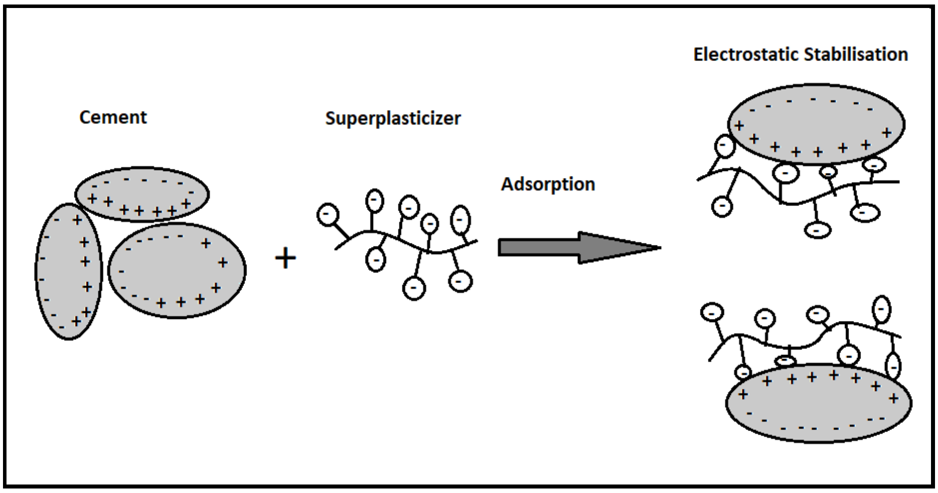


Figure 2.5.1.1 Electrostatic repulsion forces

Once this layer is formed, additional positive ions are still attracted by the particle, but on the other hand, the Stern layer, which is filled with positive charges, repels these charges. In this dynamic equilibrium, positively charged “diffuse layer” is formed just outside the stern layer. The positively charged ion concentration decreases and the negatively charged ion concentration increases as it moves away from the particle until equilibrium is reached. These two layers are generally referred to as “double layers. The thickness of this layer varies depending on the ion type and concentration[29].

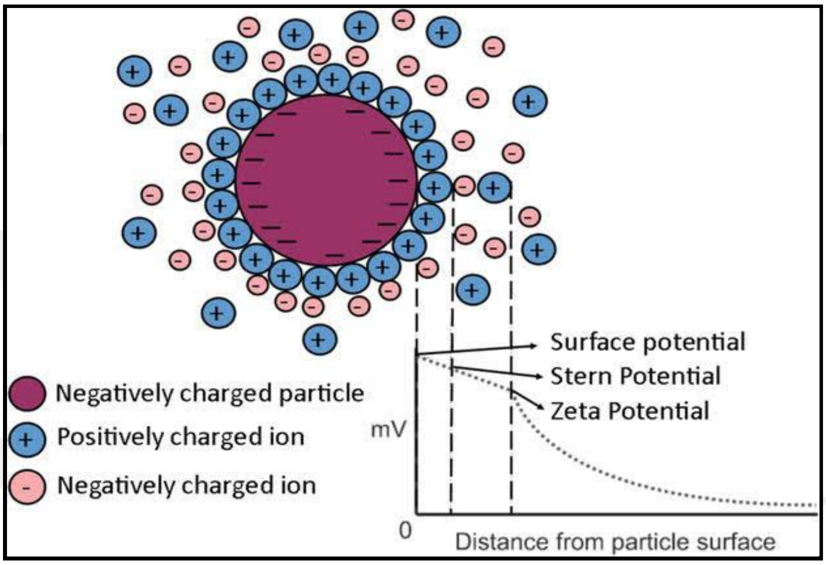


Figure 2.5.1.2 Dual-layer model[29]

Lignosulfonate, naphthalene and melamine-based superplasticizers disperse cement particles by electrostatic propulsion mechanism. In practice, these admixtures based on electrostatic stabilization can provide sufficient workability of the concrete for a period of 30 to 60 minutes. then, the attraction of van der Waals leads to a re-agglomeration of cement particles[30].

Electrostatic repulsion between cement particles is determined by Zeta potential measurement. Polymers give a negative charge to repel each other after adsorbing on the surface of the cement particles. This charge is the zeta potential of the dispersant and explains the ability of the cement particles to affect other charged cement particles in the suspension (Figure 2.5.1.2) [31].

2.5.2. Steric Hindrance

Uchikawa et al stated that one side of the polymer chain is adsorbed on the surface of the cement grain, while the long non-adsorbed side creates steric repulsion by creating a physical barrier between the compounds and this phenomenon is illustrated in the figure below Figure 2.5.2.1[32].

Polycarboxylate polymers have a high molecular weight due to a lot of carboxylic groups and polyoxyethylene side chains. This creates a steric effect with long side chains when polycarboxylate superplasticizers are used and they can provide sufficient workability over a period of 60 to 90 minutes. Other lignosulfonate, sulfonated naphthalene sulfonated melamine-based superplasticizers have a lower molecular weight than the polycarboxylate superplasticizers and have no long side chains, so no steric effect is observed[32, 33].

The most important parameters affecting steric repulsion are adsorption layer thickness and solid liquid interface. In addition, the degree of backbone polymerization of the chemical structure of the polycarboxylate type superplasticizer used, the composition of functional groups such as polyoxyethylene (PEO) side chain length, carboxylic and sulfonic groups, and the purity of the polymers are the properties that determine the characteristics of the steric effect[31, 33].

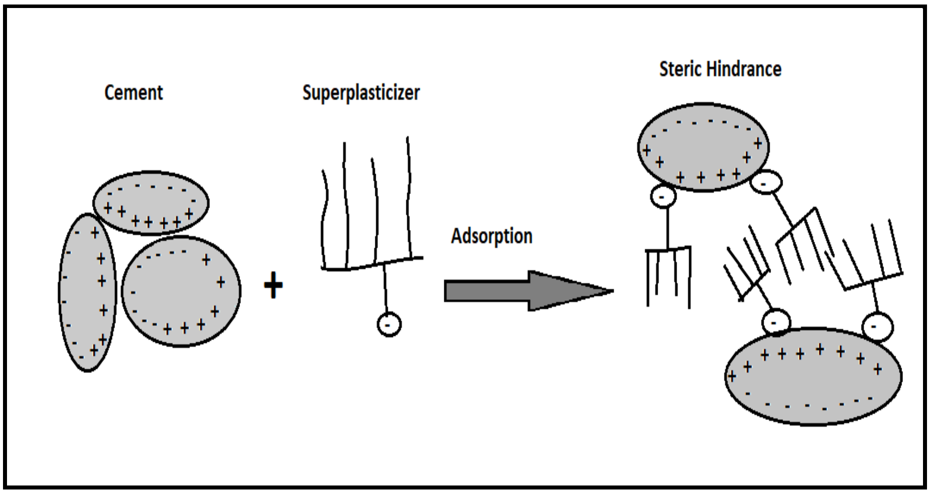


Figure 2.5.2.1 Steric hindrance

2.6 Compatibility Superplasticizer with Cementitious Systems

As a result of the production and widespread use of high-performance concrete, compatibility of superplasticizer and cement has become an important problem. In order to observe the compatibility, in literature studies, important factors are mentioned about workability properties of low water-binder ratio in fresh concrete. The common view of these studies is the chemical composition, structure, molecular weight, admixture form and order of the admixture, and the factors affecting the cement- admixture interaction[34].

According to M. Akman et al., the presence of superplasticizers and the lack of water leads to different hydration products and changes in internal structure morphology. At the end of these changes the setting and curing times, the value of the hydration temperature and the speed differ and this is defined as the incompatibility of the cement and superplasticizer[35, 36].

According to Rana et al. (2009), with increasing side chain length, admixture performance increased due to increased steric effect[37, 38]. According to Mardani Aghabaglou et al. (2013), the increase in admixture side chain density to a certain value was observed to improve the fresh state properties. However, they stated that after a certain density, the workability of fresh concrete was adversely affected, possibly because the side chains blocked each other[39].

Since the length of the side chain increases proportionally with the molecular weight, it has been reported that the admixture performance increases with an increased molecular weight of sulphate polystyrene-based, sulphonate melamine formaldehyde-based, sulfonated naphthalene formaldehyde-based, polycarboxylate-based admixtures. They also stated that it has the highest performance in terms of workability at an optimum molecular weight[40-42].

According to J. Golaszewski, the addition of the admixture significantly affects the compatibility of the cement and superplasticizer. Hence, the effects of the pozzolanic addition and superplasticizer properties are impressively observed on the setting time and compressive strength of the mortars[43].

2.7. The Role of Superplasticizer on Sustainability of Concrete

Plasticizers are chemicals that reliably increase the sustainability of a wide range of cementitious systems. These admixtures are added to the concrete in very low amounts and mostly in liquid form before or during mixing, resulting in a reduction in CO_2 emissions [13].

It is known that selecting the most compatible cement-admixture for each mixture has a positive effect on the fresh and hardened properties of the mixture. The use of superplasticizer in concrete causes a decrease in the amount of cement used per unit MPa in concrete. The decrease in cement consumption has a positive effect on conservation of natural resources and energy consumption[44, 45].

In addition, when pozzolana is used in the cement mixture, the fluidity can be kept at the desired level and the cement content can be further reduced. J.Golaszewski stated that the use of polycarboxylate-based superplasticizer leads to an increase in the desired metakaolin content in cement[43, 46].

2.8 Humic substances and Their Properties

2.8.1. Humic substances

Humic substances are high molecular mass compounds which form molecularly flexible polyelectrolytes, and these brown or black materials are components of houmous. These are amorphous organic substances that contain carbon, hydrogen, oxygen and some sulfur together with nitrogen, which are formed in soil, sediments and aqueous environments during the physical, chemical and microbiological transformation process of dead animals and plants[47].

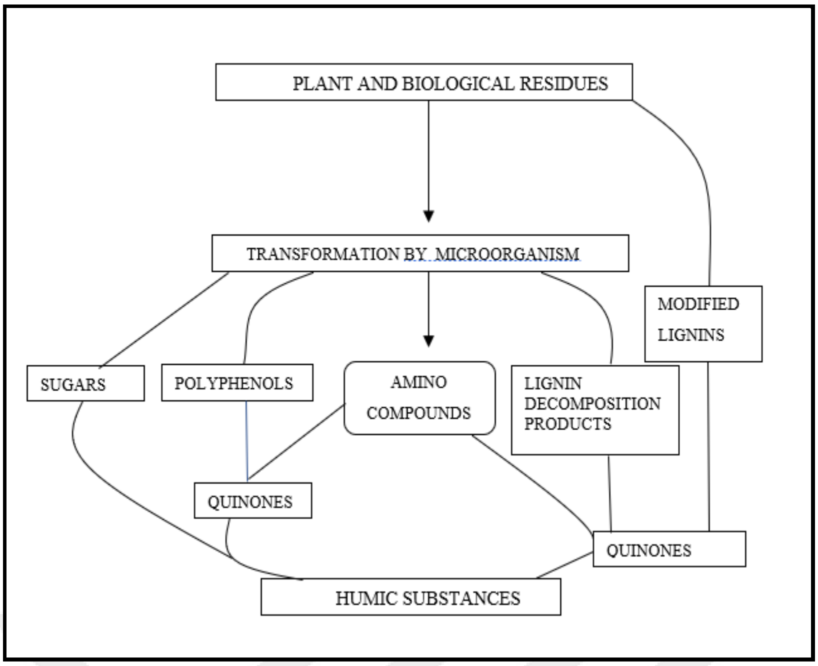


Figure 2.8.1.1 The formation of humic substances [48]

Formation of humic substances from organic substances is defined as ‘humidification’ and these substances can be found in various environments such as coal, lake, river and soil and have a complex chemical structure which can be defined as biopolymer [49]. The formation of humic substances is based on 4 theories (Figure 2.8.1.1): lignin modification, quinone amino acid interaction, microbial synthesis of aromatic and mallard reaction (a sugar amino acid reaction). Each of theory explains complex biotic and abiotic reactions in which various organic compounds are re-synthesized to form large complex polymers. They show alterations in their molecular properties depending on the environmental conditions in which they are formed. Some of the typical molecular components of these substances are polysaccharides, lignins, polypeptides, ketal, fatty acids, esters, phenols, lipids, carbonyls, quinones, peroxide, benzene, ethers, acetal, aliphatic (carbon chains) compounds and lactol, furan ring compounds [50, 51].

Humic substances are mainly composed of three main components, humin, humic and fulvic acids as shown in Figure 2.8.1.2. These subsections are based on the aqueous solubility of each acid at different pH levels. Humins are insoluble in water at any pH, fulvic acids are water soluble at all pH and humic acids are insoluble in water when the pH is below 2.

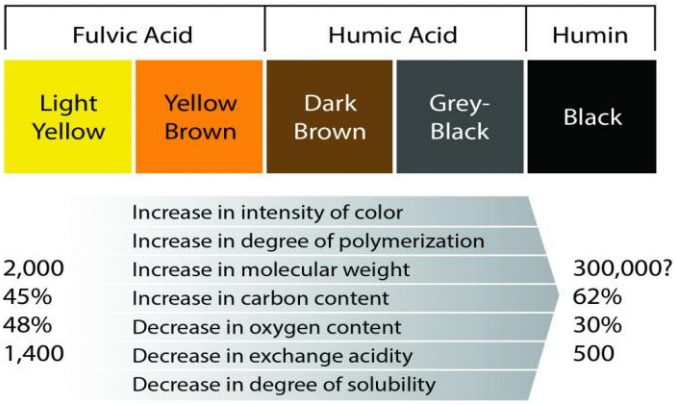


Figure 2.8.1.2 Chemical properties of humic substances [48]

Humins are macro-organic materials because of their molecular weights of between 100,000 and 10,000,000. The chemical and physical properties of these materials are not fully understood. It is the most resistant to decomposition compared to other humic materials in soil. Its main function in soil is to improve soil fertility by improving soil structure, increasing water holding capacity of soil, providing soil stability, working as a cation exchange system. Humin, which provides all these, is an important component of fertile soil [51].

Humic acids consist of 65%weak aliphatic carbon chains and 35% aromatic carbon rings which are soluble in water only under alkaline conditions. In aqueous humic material solution, pH can be lowered below 2 and humic acid can be obtained by precipitation. Humic acids have a molecular size of about 10,000 to 100,000. It is believed that the carbon-containing compounds are flexible linear polymers in the form of random coils with cross-linked bonds. Naturally occurring humic acids contain over 60 different mineral elements. Although the exact structure of humic is undefined due to the abundance of influencing factors, the proposed general structure model is shown in Figure 2.8.1.3. Humic acid easily form salts with trace mineral elements (iron, zinc, copper, magnesium; manganese, iodine, cobalt, fluorine, selenium, chromium etc.). These substances contain these trace elements in a form that can be easily used by various living organisms. As a result, humic acids form chelating systems with highly functional groups and metal cations [51, 52].

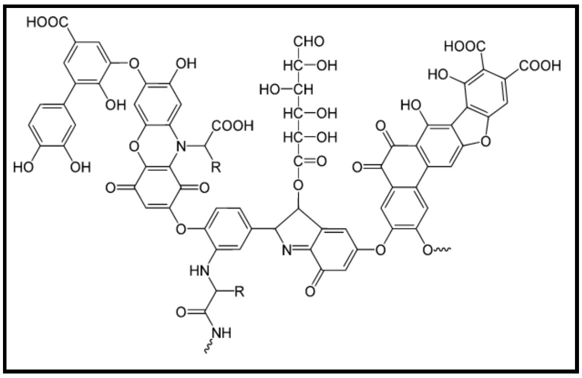


Figure 2.8.1.3 Simplified molecular structure of humic acid [48]

Fulvic acids consist of weak aliphatic and aromatic organic acids that are soluble in water at all pH conditions (acidic, neutral and alkaline). Molecular compositions, shapes are highly variable and the proposed molecular structure is as in Figure 2.8.1.4. These materials have an about 1,000 to 10,000 molecular weight and have twice as much oxygen as humic acids. Since many carboxyl (COOH) and hydroxyl (COH) groups are present, fulvic acids are more chemically reactive. Due to the total number of carboxyl (COOH) groups present (from 520 to 1120 cmol (H^+) / kg), the exchange capacity of fulvic acids is more than twice that of humic acids. Fulvic acids show no evidence of methoxy groups (CH_3) groups in some analyzes. They are also less aromatic in molecular structure than humic acids. Because of the molecular size of fulvic acid, it can easily penetrate into plant roots, stems and leaves and thus carry trace minerals from plant surfaces to plant tissues. Fulvic acids are essential components of high-quality leaf fertilizers. fulvic acid mineral chelates, foliar spray applications in certain plant growth stages to maximize the production capacity of plants [51].

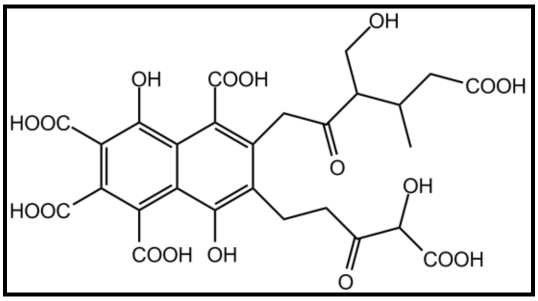


Figure 2.8.1.4 Simplified molecular structure of fulvic acid [48]

Higher productivity was obtained in the studies carried out on soils with a rich composition of humic substances. However, humic or fulvic acid is defined as soil regulators and is not accurate to use as direct fertilizer [52].

2.8.2 Extraction of humic substances

Studies on the components of organic substance require extraction of fully decomposed houmous from the soil, followed by isolation and purification of the houmous fractions. By extraction of organic matter, humic substances can be separated into fractions according to their solubility characteristics. The most important source for humic acids is leonardite which is formed by high oxidation of lignite during carbonization. This material is in the form of solid granules, which improves the physical and chemical features of the soil, increases the biological activity, and contains highly humic acids. Some chemical substances such as KOH or NaOH can be used to obtain high levels of humic acid (85%) by different extraction processes. Firstly, as a result of the extraction of soil or sediment with alkali, insoluble (humin) and soluble (humic acid + fulvic acid) is obtained. When the dissolved part is treated with acid, two parts are obtained which are precipitated (humic acid) and non-precipitated (fulvic acid). The stages of humic and fulvic acid obtained from leonardite are obtained in Figure 2.8.2.1[53].

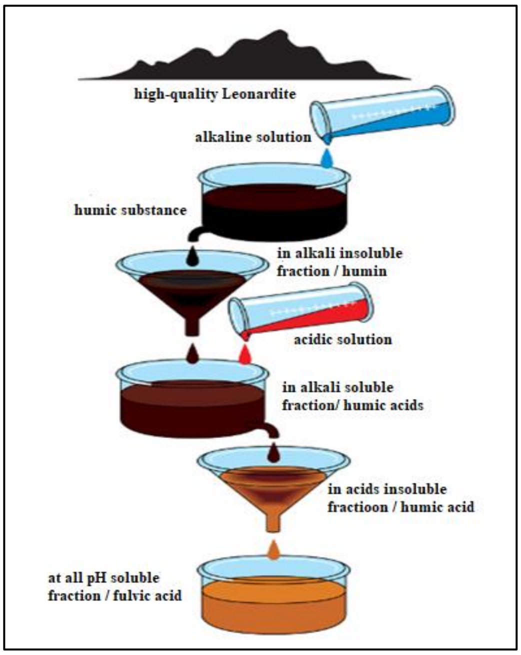


Figure 2.8.2.1 Isolation humic acid and fulvic acid[53]

2.8.3 Properties and Applications of Humic Substances

2.8.3.1 Fertility in Agriculture

Humic substances are one of the most important carbon reserves in nature and 80% of the total carbon in nature is in humic substances. These provide most of the energy and mineral requirements for soil microorganisms and soil animals. These beneficial soil organisms (bacteria, algae, yeasts, fungal nematodes, mycorrhiza and small animals) play an important role in plant health and soil fertility. The important function of humic substances are increasing the water retention capacity in soil. In particular, it helps to form the soil structure that keeps water in the root zone. These materials are capable of holding up to seven times its volume in the water thanks to its large surface area and internal electric charge. The water, which is held in the upper soil, forms a nutrient carrier area for plant roots and beneficial soil organisms[51].

Excessive fertilization, anhydrous ammonia applications and other destructive applications reduce the residence time of humic substances in the soil. The turnover period of organic carbon added to the soil from plant and animal remains is approximately 30 years. Nowadays, in order to restore the health of the soil, growers need to make production practices that prevent the disintegration of humic substances in order to keep the soil content high[53].

The degradation of soil fertility is increasing and needs innovation to improve soil fertility. In response to this innovation, Niken stated that humic acid is an alternative material that can be used to support cultivation production. In this study, the effects of humic acid on the growth of coffee seedlings were investigated. Comparative effects were observed using three different dosages (0 g, 10 g and 30 g for 2 kg of dry soil) of humic acid, coffee pulp compost and fertilizer. As a result, it was found that humic acid significantly increased plant properties and humic acid and root, stem diameter and leaf weight were better than compost from coffee extract and fertilizer [54].

Cimrin et al. investigated the effect of soil nitrogen, phosphorus and potassium fertilizer combinations and humic acid applications on the development and mineral nutrition of corn. In the study, a solid regulator which contains 85% humic acid was used. Humic acid applications together with fertilizer combinations significantly increased the dry weight of corn plant and N, P, K, Fe, Zn and Mn contents of the plant and decreased Ca and Mg contents. K, Ca and Mg contents of the plant decreased and Fe content increased significantly only when humic acid was applied[54].

Pagel and Dixit and Kishore as a result of their work; reported that humic acid content increased the enzymatic activities in seed tissues during germination and encouraged the germination of seeds of various plant species and increased germination rate and also positively affected the root and above ground growth of plants[55].

2.8.3.2 Water Treatment

Heavy metals are not biodegradable and accumulate in living tissues, causing great harm to both human health and the ecological environment. Common heavy metals are, arsenic, cadmium, cobalt, lead, chromium, zinc, copper, nickel, mercury, etc. and these metals can cause toxicity to human health and cause serious side effects such as gastrointestinal problems, hair loss, hypoglycemia, nausea kidney damage, anaemia, severe headache and even death. As a result, the need to remove heavy metals has become a necessity. Various methods such as coagulation, membrane filtration, chemical precipitation, reverse osmosis, solvent extraction, flotation, ion exchange and adsorption have been used to remove heavy metals from water[56-59].

Humic acid and fulvic acid are complexed with metal ions in aqueous media thanks to various functional groups and then interact with nanomaterials. Nanomaterials play an important role in this stage due to their large surface area and high reactivity. These interactions and subsequent mechanisms with carbon-based nanomaterials, iron-based nanomaterials and photocatalytic nanomaterials allow the removal and transport of heavy metals from aqueous solutions[59].

Liu et al investigated the use of as adsorbents for the absorption of Co (II) from aqueous solutions. The effects of absorption, contact time, pH, foreign ions, fulvic acid, humic acid and temperature parameters were observed. Finally, the presence of fulvic acid and humic acid was reported to increase Co (II) absorption in multi-walled carbon nanotubes compositions at low pH[60].

Likewise, another study examines the adsorption of the compound formed with humic acid and Pb (II) to polyacrylamide. By examining the different effects of humic acid and Pb (II) concentrations and the additional sequences of Pb (II) and humic acid adsorption, the adsorption mechanisms are indicated in the Figure 4.1.3.2. [61].

Lastly, the presence of humic substances in ternary systems consisting of humic acid and fulvic acid and TiO_2, multi-walled carbon nanotubes increased the photocatalytic reduction. further, the adsorption of humic substances and Cr (VI) compounds to TiO_2 / multi-walled carbon nanotubes increased [62].

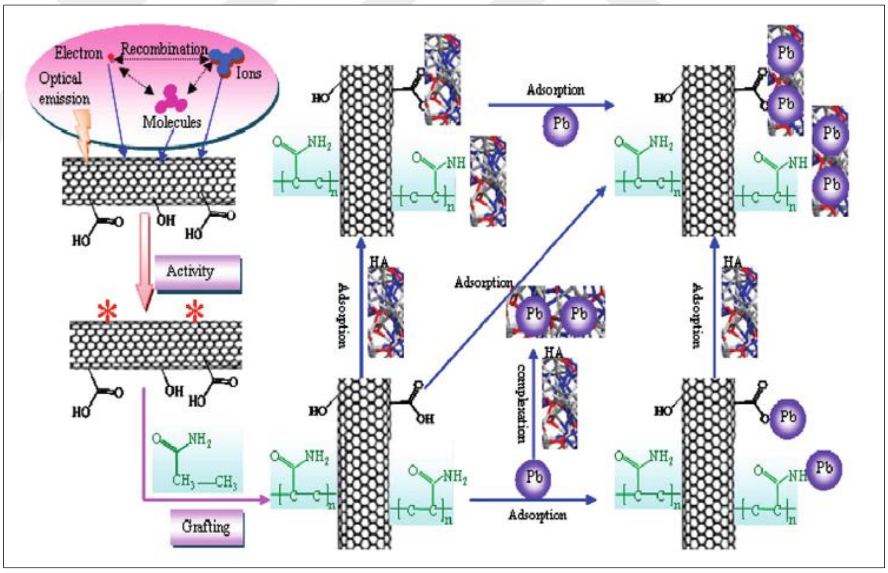


Figure 2.8.3.2.1 Proposed schematic adsorption mechanisms of Pb (II) and humic acid on multi-walled carbon nanotubes polyacrylamide [62]

2.8.3.3 Medical Applications

Many studies in the literature have reported that humic acids play an important role in the treatment of many diseases and have investigated their medical properties. Humic acid molecules that take a negative charge in a neutral environment can prevent virus proliferation by binding the cationic sites necessary for binding of the virus to the cell surface. This antiviral activity role of humic acid was observed against cytomegalovirus (CMV), vaccine viruses, human immunodeficiency virus type 1 (HIV-1) and type 2 (HIV-2) [63, 64].

Humic acid has a positive effect on wound healing and antibacterial properties according to Çalışır et al. In this study, humic acid treatment was superior to chlorhexidine gluconate, which is commonly used for the healing of oral wounds[65].

Humic acids are known for their antiviral and UV-visible protection in sunlight, anti-ageing and skincare products. Klöcking et al. produced a UV-protecting lipstick to minimize or even prevent recurrence of herpes simplex virus-induced cold sores. They indicated that humic acid can be used as components of functional lipsticks because humic acid at concentrations higher than 100 −g ml^{-1} can protect U937 cells from UV-induced damage[66].

2.8.4 Humic Acid in Cementitious Systems

The number of studies on the effect of humic acid on the cementitious system is quite limited in the literature.

Robertson and Rashid (1976) in Portland cemented concrete investigated the corrosive effect of humic acid on freshwater and saline environments with a concentration of 10 ppm organic matter. The most abundant calcium cation in the concrete was released in fresh and saltwater systems with humic acid at concentrations of 28 and 96 ppm. As a result, they observed that the humic components found in aqueous or sedimentary environments had no adverse effects on the concrete structures. On the contrary, they found that humic material forms a protective cover on the concrete block surface[67].

According to K. Kılınç, and S.G. Gök, the pollution of aggregates, which has a high methylene blue value, causes problems in workability and compressive strength of concrete. The aim of this study is to increase the slump value or decrease the cement content by using new special chemical admixtures based on humic acid with aggregates having high methylene blue values. The compressive strength test of concrete mixtures prepared with different aggregate types was applied at different ages. It has been observed that by adding humic acid to these concrete mixtures, it eliminates the negative effects of clay containing aggregates [68].

Multi-walled carbon nanotubes (MWCNTs) are materials used in cement due to their superior material properties. However, the efficiency of this application depends on the distribution of MWCNTs. In this study, humic acid was used to stabilize the dispersion degrees of MWCNTs in alkali cement medium. The activity of humic acid here was characterized using an ultraviolet spectrophotometer. As a result, 0.12% by weight added to MWCNT suspensions was found to be the optimum value to improve the humic acid distribution. The Zeta potential results (-42 mV) obtained by Fabiana de Souza show that humic acid has a significant surface charge density in the alkaline environment. However, at acidic pH, the molecules are prevented from being dissolved and thus do not function as a dispersant. [69]

Chapter 3

Experimental Study

3.1. Materials

3.1.1. Portland Cement

In this study, CEM I 42.5-R type Portland cement complying with TS EN 197-1 standard was used in the study. Chemical, physical and mechanical properties of cement are given in Table 3.1.1.1 and Table 3.1.1.2, respectively.

Table 3.1.1.1 Chemical analysis of Portland cement

Chemical Composition (%)	
SiO_2	17.78
Al_2O_3	4.59
Fe_2O_3	3.73
CaO	62.94
SO_3	4.87
MgO	2.41
Na_2O	1.08
K_2O	1.00
TiO_2	0.34
CuO	0.10
MnO	0.07
P_2O_5	0.07
Loss on ignition	1.00

Table 3.1.1.2 Physical properties of the cement

Properties	Values
Specific gravity (g/m^3)	3.13
Specific surface(kg/m^3)	3469
Setting time start(min)	212
Setting time end(min)	316
Residue on 45µ sieve (%)	4.8
Residue on 90µ sieve (%)	0.5
Compressive Strength	
2 days (MPa)	23.7
28days (MPa)	46.5

3.1.2. Sand

River sand is used in preparation of mortar mixtures. The river sand used is 0-3 mm in nominal size and its sieve analysis is given in Figure 3.1.2.1 in comparison with the standard sand in according to with EN 196-1[70].

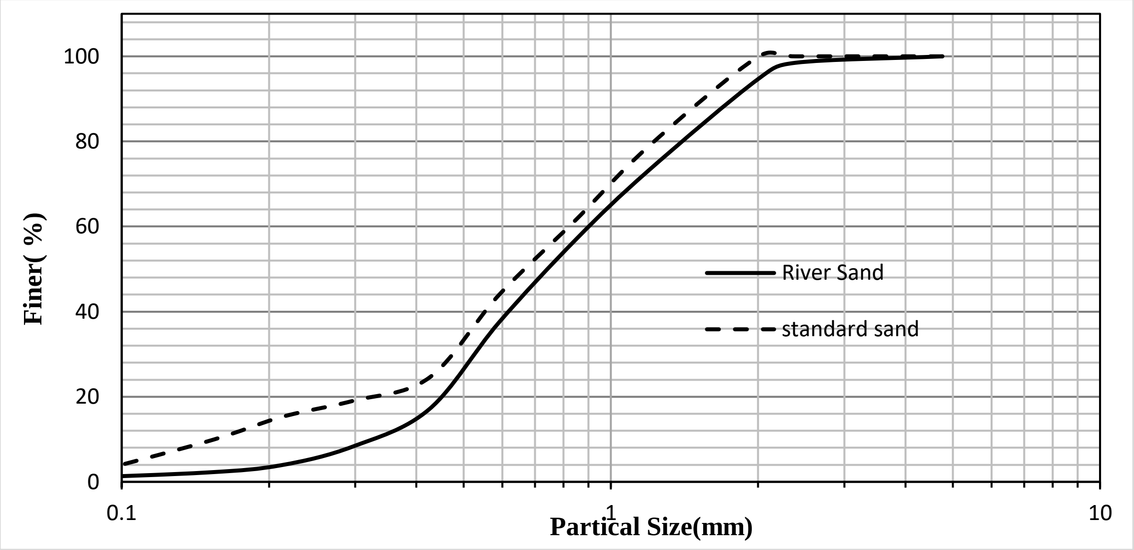


Figure 3.1.2.1 Particle size of standard sand and river sand

3.1.3. Water

Potable tap water from the city network was used in sample production. According to TS-EN 1008 standard[71], it is indicated that potable water can be used as mixing water.

3.1.4. Superplasticizers

In this study, commercially available humic acid solution obtained from leonardite was used. This solution was compared with two superplasticizers which are based on lignosulfonate (LS) (0.4%-1% dosage range recommended by the producer), and naphthalene formaldehyde sulfonic acid (NA) (1% to 2% dosage range recommended by the producer). The technical properties of commercial superplasticizer and HA-based solution are shown in Table 3.1.4.1. The chemical composition of the LS-based and NA-based superplasticizers and humic acid-based solution in dry powder form obtained with XRF analysis is shown in Table 3.1.4.2.

Table 3.1.4.1 Technical properties of superplasticizers and humic acid-based solution

	LS	NA	HA
Active ingredients	Modified lignin sulphonate-based	Naphthalene sulphonate-based	Naphthalene sulphonate-based
Colour	Brown	Brown	Brown
Density (kg/liter)	1.122- 1.182	1.154-1.124	1.097
Chloride Content%	<0.1	<0.1	<0.1
Alkaline Content%	<10	<10	<10

Table 3.1.4.2 Chemical Composition s of Superplasticizers (%)

	LS	NA	HA
SiO_2	0.07	0.08	2.05
Al_2O_3	-	-	1.82
Fe_2O_3	-	-	3.03
CaO	14.9	0.72	4.52
MgO	0.13	0.08	0.20
SO_3	6.21	39.4	5.76
K_2O	5.78	0.11	35.7
Na_2O	8.99	21.0	-
Cl^-	1.43	0.08	-
TiO_2	-	-	0.14
Na_2O+0.658 K_2O	12.8	21.1	23.5
Loss on ignition	62.5	22.0	46.3

It should be noted that the total alkaline solid part of HA-based solution was found to be comparable with that of NA-based superplasticizer

3.2. Methods

The usage dosage of LS, NA and HA-based superplasticizers and nano silica in cement mixtures are shown in Table 3.2.1. The cement mixtures were prepared according to ASTM C1329/C1329M [72]. Their sand to cement ratio is 1:2.75, water/binder ratio of cement paste and cement mortar are 0.4 and 0.5, respectively. While preparing cement mixtures, superplasticizers was mixed with mixing water and added to the mixture. All mortar test samples were prepared with a laboratory mixer as in Figure 3.2.1.

Figure 3.2.1 Laboratory mixer

Table 3.2.1 Mixtures of Experiments

No	Cement Notation	Nano Silica (%)	Superplasticizers (%)
1	PC	–	–
2	LS 0.5	–	0.5
3	LS 1.0	–	1.0
4	LS 1.5	–	1.5
5	LS+NanoSilica	5	1.5
6	NA 0.5	–	0.5
7	NA 1.0	–	1.0
8	NA 1.5	–	1.5
9	NA+NanoSilica	5	1.5
10	HA 0.5	–	0.5
11	HA 1.0	–	1.0
12	HA 1.5	–	1.5
13	HA+NanoSilica	5	1.5

3.2.1. Isothermal Calorimeter Test

The isothermal calorimeter measures the heat flow of the sample by comparing with the reference material and keeps the sample and the environment at a constant temperature. The material placed in the reference container of the device must be of equal heat capacity with the material to be placed in the sample container (Figure 3.2.1.1).

The calorimetric channel was designed in a twin configuration, for sample and reference, as in Figure 3.2.1.2. In this setup, there are two heat flow sensors, one below the sample and the other below the reference.

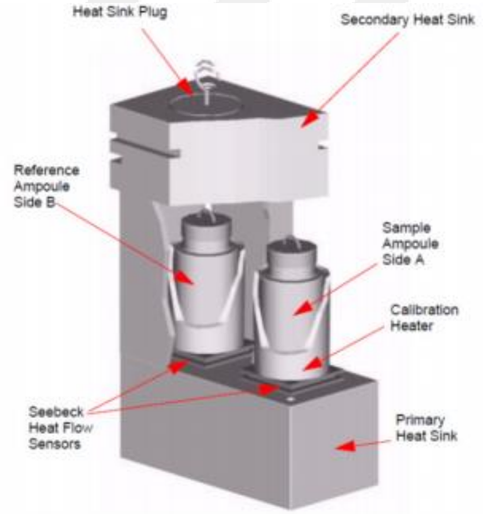


Figure 3.2.1.1 Twin configuration of calorimetry from isothermal calorimeter[73]

The heat flow from these sensors generates a proportional voltage signal, which is reflected on the device monitor. Thus, heat flow of cement paste samples is observed and measured over time. By integrating the measured heat flow graph, the total temperature of the hydration is calculated according to ASTM C1679 standard[74].

20 g of the mixture was prepared for each mixture and prepared manually with the help of a spatula. In the preparation of paste for each mixture 0.40 water/cement ratio is used. Immediately after preparing the cement paste mixtures, the sample was filled into ampoules and put into the device. Heat flow of these samples was recorded for 80 hours.

Figure 3.2.1.2 Isothermal calorimetry and ampules of samples

3.2.2. Thermogravimetric Analysis of Cement Pastes

The free $Ca(OH)_2$ content of hardened cement pastes prepared with 0.4 water-cement ratio and different superplasticizers were determined by Thermogravimetric Analysis at 3,7,28 days. These pastes prepared with deionized water by using a hand mixer. After the mixture became homogeneous, the cement pastes were placed in plastic syringes and the ends of the syringe were closed with lids to prevent moisture loss and carbonation Figure 3.2.2.1. Then, these samples were kept at room temperature until the day of the experiment.

Figure 3.2.2.1 Syringes with cement pastes

When the test days of the samples arrived, they were removed from the syringes and ground in a suitable container. Then the samples are taken to the TG/DTA Shımatzu device and the samples are raised up to 1000 ˚C from room temperature at the heating rate of 10˚C/min. At the end of the experiment, the desired free $Ca(OH)_2$ content was reached at approximately 450˚C of the graph.

3.2.3. Flow Table Experiment

In order to observe the effect of admixture on workability, flow table test was performed according to ASTM C1437 - 01[75]. The flow values of cement mortars were obtained comparatively by using at different dosages plasticizing and nano silica.

Figure 3.2.3.1 Flow table

3.2.4. Setting Time Experiment

Setting Time test is made in accordance with standard ASTM, "C230/C230M-14[76]. In this experiment, the paste sample is prepared and placed in the vicat mould (Figure

3.2.4.1). One of the important points is that the surface of the paste placed in the mould is flat. According to the properties of the mixture, every 10, 20 and 30 minutes the needle was dipped in the cement paste sample. In this way, start and finish setting times have been reached.

Figure 3.2.4.1 Vicat apparatus

3.2.5. Compressive Strength

The samples were then poured into three-chamber steel cube moulds of 50x50x50 mm. These moulds were lubricated before casting the samples so that the samples would not come out of the moulds more easily and would not be deformed. In order to compress the mixture well during casting, the casting was made in two layers and was placed on the shaking table (TS EN 196-1 [70]) after casting of each layer.

The water/cement ratio was 0.5 in the mortar mixtures and 0.4 in the paste ones. The samples were cured by covering the moulds with plastic stretch film and a wet cloth to prevent water loss for 24 hours after pouring.

After 24 hours, the samples were carefully removed from the moulds and keep in cure at room temperature (21 ± 1°C) in water. Samples were tested at days 3, 7, 28.

Figure 3.2.5.2 Hydraulic compression machine

Compressive strength of hardened cubic specimens was determined in accordance with TS EN 1015-11[77]. This test was carried out on 3 or 6 samples from each mixture using a hydraulic compression machine (Figure 3.2.5.2) at 3, 7 and 28 days of age. A constant loading rate of 500 N/s was selected. The compressive strength values were computed from averages of these samples were taken.

Chapter 4

Results and Discussions

In this section, the data obtained from experimental studies on cementitious systems containing various dosages of different superplasticizers are presented. The results were the results for the superplasticizers used in the study were evaluated comparatively each other as well as the literature.

4.1. Isothermal Calorimetry Test

According to ASTM C 1679, cement pastes prepared with a water/cement ratio of 0.4 were analyzed in isothermal calorimetry and heat flow, released heat of hydration are determined.

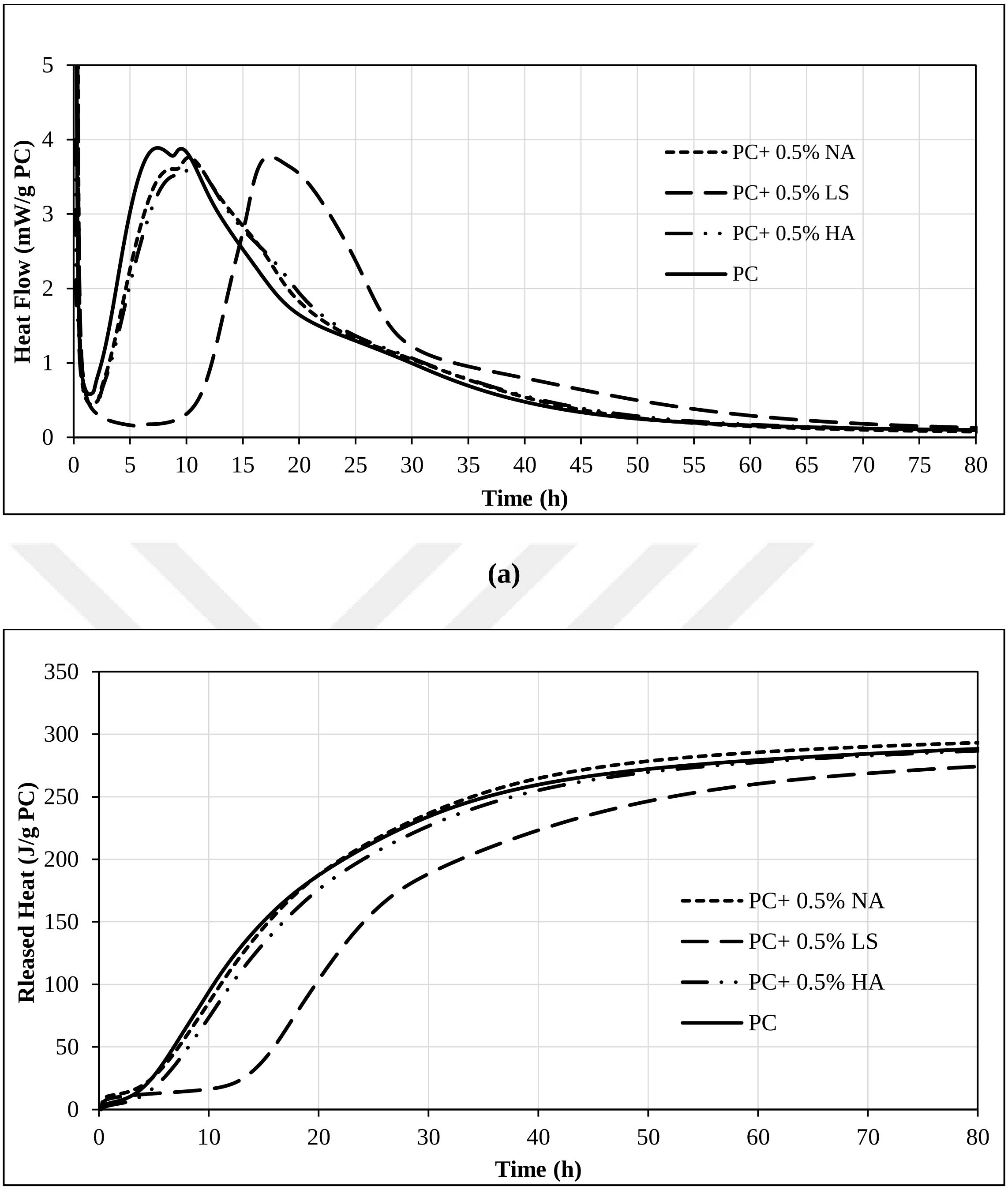
The presence of a superplasticizer has a reaction retarding effect by shifting the initial reaction to the right at all applied dosages as seen in Figure 4.1.1 (a) in Figure 4.2.1 (a) in Figure 4.3.1 (a). At a dosage of 0.5 %, the initial reaction time of the control sample is 1 hour, while the reaction time of the others with HA-based and NA-based samples is approximately 2 hours as shown in Figure 4.2.1 (a). However, the reaction time of the sample with LS lasted up to 10 hours. Reaction retarding effect of LS-based sample is the most evident even at the lowest dose used in Figure 4.3.1 (a). Due to this effect, LS-based concrete mixtures are not suitable for early strength. At dosages of 1.0% and 1.5%, this delay becomes more pronounced in Figure 4.1.2 (a) and Figure 4.1.3 (a).

The initial peak of the control sample appeared at around 8 hours regardless of the presence of superplasticizers but initial peaks of sample with LS, NA and HA-based superplasticizers occur later. The increase in the use dosage also causes a delay in peak formation as shown in Figure 4.4.1 (a) in Figure 4.2.1 (a) in Figure 4.3.1 (a). When the total hydration rate of 0.5% in Figure 4.1.5 (b) is considered, the NA-based sample 51 captured the control sample at 20 hours and HA-based sample captured at 45 hours. In Figure 4.1.2 (b), at 1.0% dosage, the released hydration rate of HA and NA-based admixtures is approximately equal to that of the control sample and is 40 hours and 50 hours, respectively. In Figure 4.1.3 (b), this gap between HA and NA-based admixtures increases again at a dosage of 1.5%.

As shown in Figure 4.6.1 (a) in Figure 4.2.1 (a) in Figure 4.3.1 (a), HA, LS and NA-based admixtures, the sulfate depletion point shifts to the right. While the sulphate depletion point of the control sample was 8.92 hours, the sulphate depletion points of the NA and HA-based samples were at 0.5% dosage 10.6 hours and 11.2 hours respectively in Figure 4.7.1 (a); at 1.0% dosage 10 and 11.5 in Figure 4.1.2 (a) and at 1.5% dosage 11 hours and 11.8 hours in Figure 4.1.3 (a). This point of the LS-based samples does not show in all dosages.

The slower rate of hydration development of NS-based sample compared to other samples is explained with formation of hydration shell. Bazzoni stated that the external products formed by the reaction of the cement particle with water cover the inner products to form a hydration shell and inhibit the reaction of the inner parts of the particle [77]. This process causes the heat flow value of the hydration reaction to decrease. The subsequent hydration reaction continues slowly. Depending on the admixture material and dosage values used, the formation of the hydration shell occurs at different times. In order to see how much the hydration shell formed on the cement particles or other factors affecting the total hydration affects the total heat of hydration graph.

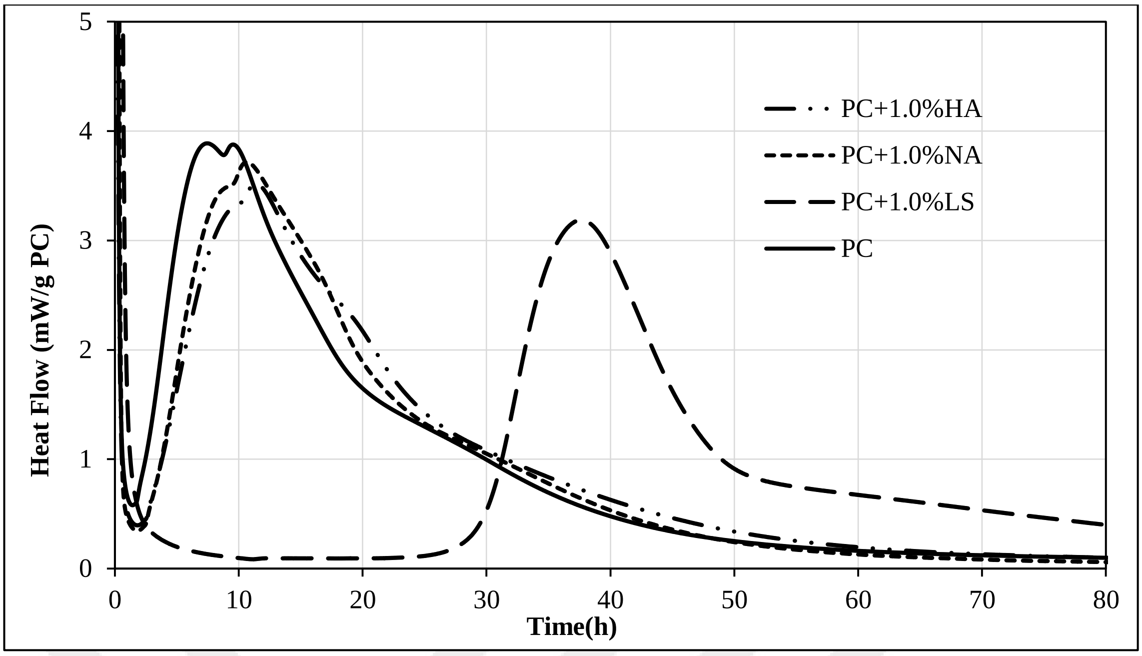
Although the first obvious delay, at a dosage of 0.5%, at the end of 80 hours, the released heat of LS-based sample close gap with the released heat value of NS and HA-based samples (Figure 4.1.1.(b)). At a dosage of 1.0%, the released heat values of HA and NA-based samples show equalization at about 53 hours, but the value of LS-based sample far from these samples Figure 4.2.1.(b)). At 1.5% dosage, the equalization does not continue between the value of NA-based released heat sample and value of HA-based sample released heat as shown in Figure 4.3.1.(b).



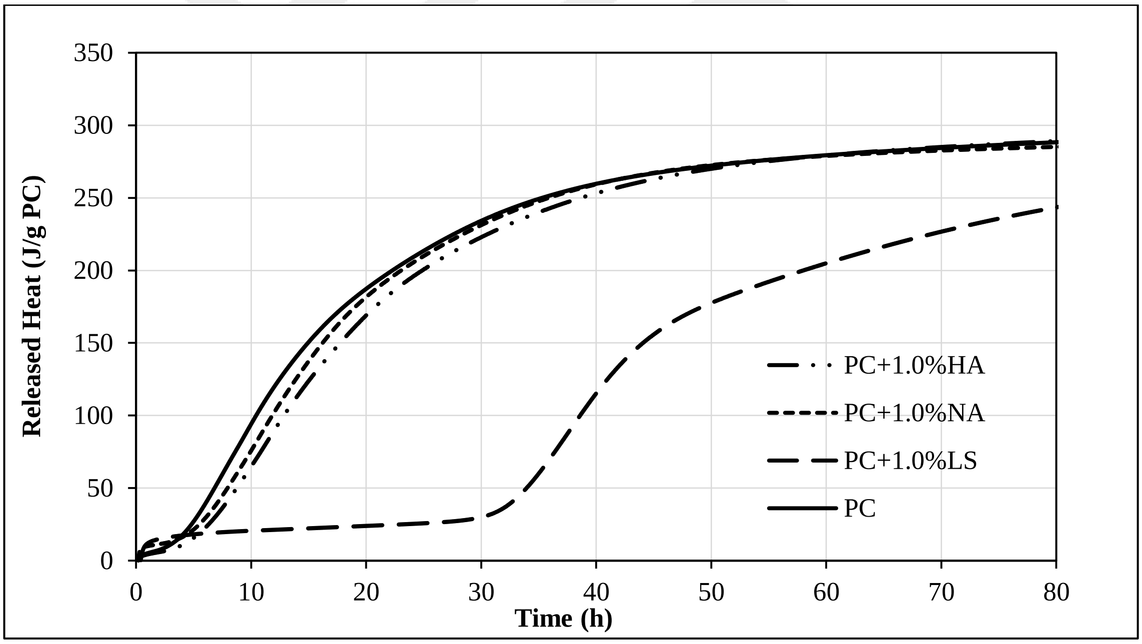
(a)

(b)

Figure 4.1.1 Heat flow and total heat of hydration for 0.5 % rate of superplasticizers

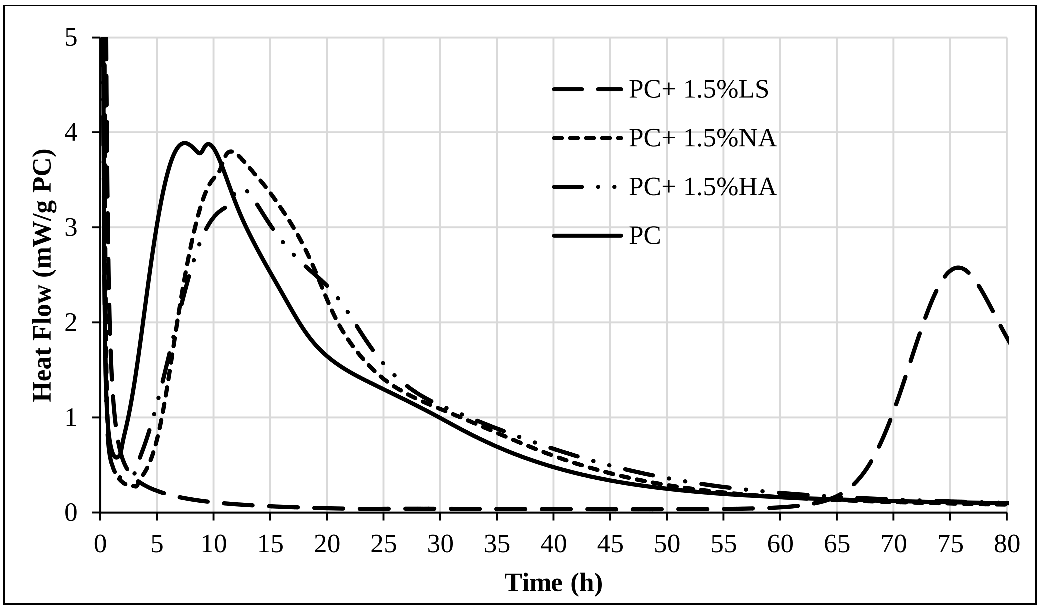


(a)

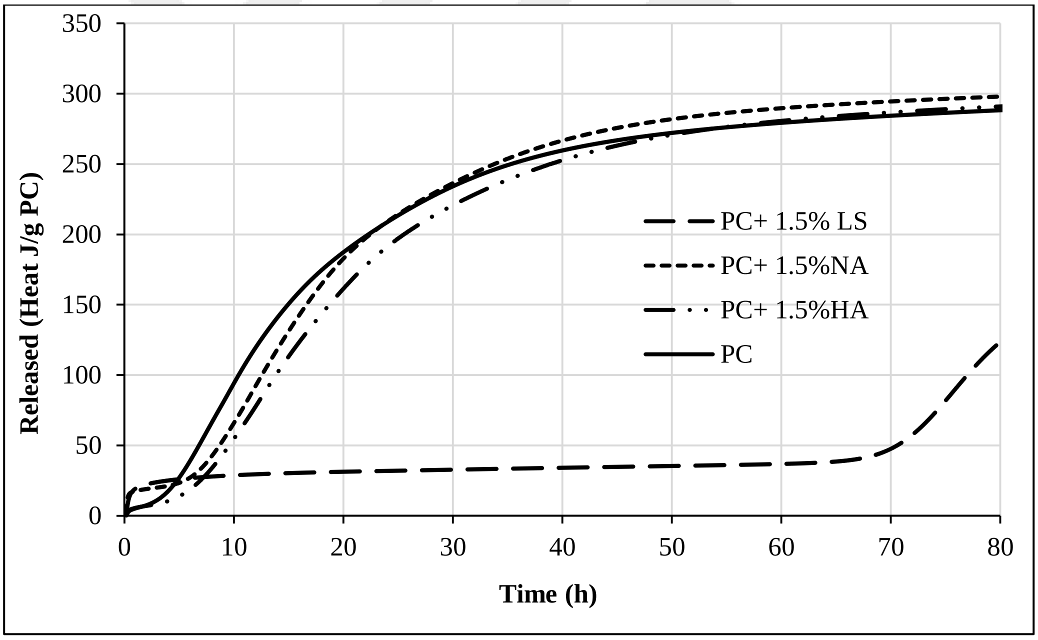


(b)

Figure 4.1.2 Heat flow and total heat of hydration for 1.0 % rate of superplasticizers



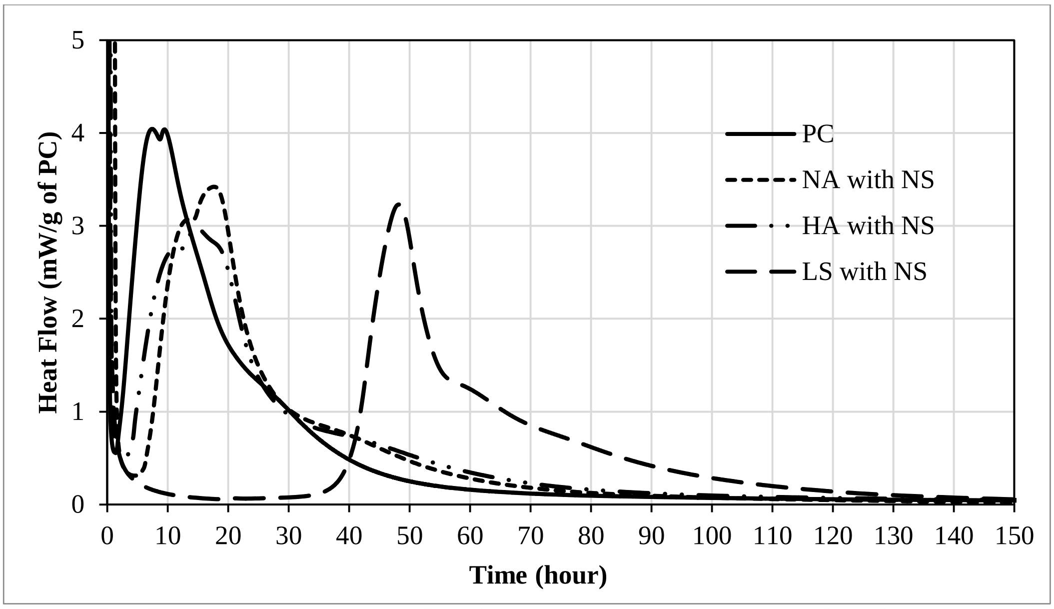
(a)



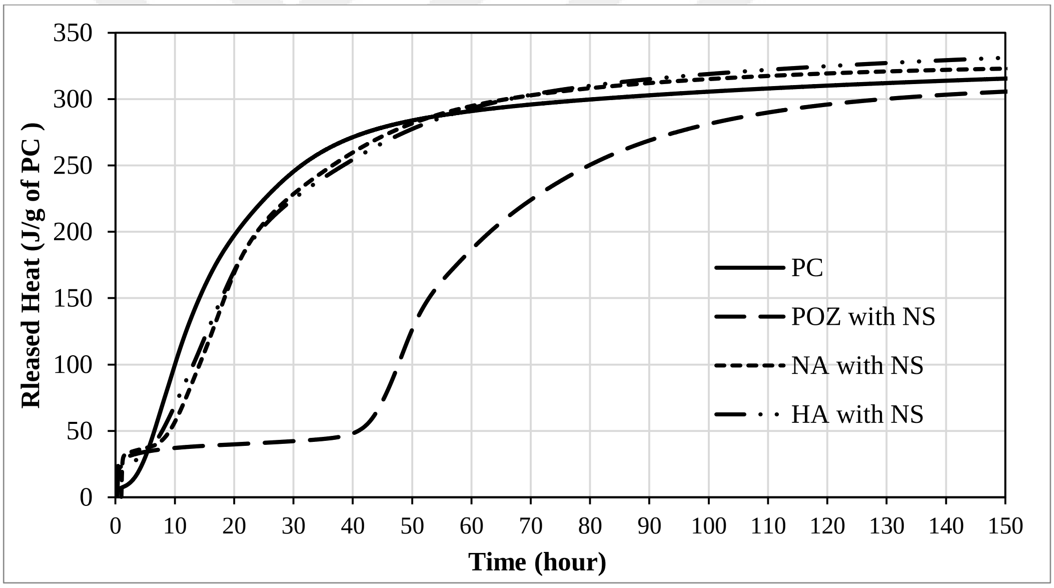
(b)

Figure 4.1.3 Heat flow and total heat of hydration for 1.5 % rate of superplasticizer

As shown in Figure 4.4.1, 5.0% replacement of nano silica with cement supports hydration due to its high pozzolanic activity. In spite of the decreasing amount of the cement, total heat of hydration value reached to non-containing cementitious mixtures.



(a)



(b)

Figure 4.1.4 Heat flow and Total heat of hydration for 1.5 % rate of superplasticizer with nano silica (NS: nano silica)

4.2. Thermogravimetric Analysis

The free $Ca(OH)_2$ amounts of in the hardened cement pastes were determined by thermogravimetric analysis and TGA plots of the hardened cement pastes are given in the Appendix. The results were obtained as percentage normalized to the ignited weight of these pastes. When nano silica is added to the cement mixture, the free $Ca(OH)_2$ content was normalized to the Portland cement content of the cementitious mixtures containing nano silica. The free $Ca(OH)_2$ content of the cementitious pastes are shown in Table 4.2.1.

Table 4.2.1 Free $(CaOH)_2$ content of the cement pastes

Cement	3-day (%)	7-day (%)	28-day (%)
PC	17.2	17.4	18.8
PC+ 0.5%LS	16.9	18.0	18.2
PC+ 1.0%LS	15.5	17.2	18.4
PC+ 1.5%LS	11.7	17.3	18.1
PC+%5 NanoSilica+1.5%LS	11.7	14.8	15.3
PC+ 0.5%NA	16.9	16.8	16.7
PC+ 1.0%NA	15.8	17	16
PC+ 1.5%NA	17.0	16.3	19.2
PC+%5 NanoSilica+1.5%NA	15.4	14.2	15.1
PC+ 0.5%HA	15.8	17.4	18.7
PC+ 1.0%HA	16.1	16.6	18.9
PC+ 1.5%HA	16.4	15.5	18.1
PC+%5 NanoSilica+1.5%HA	15.4	16.6	15.4

In order to be able to evaluate more easily, free $Ca(OH)_2$ content data in Table 4.2.1 illustrated in Figure 4.2.1.

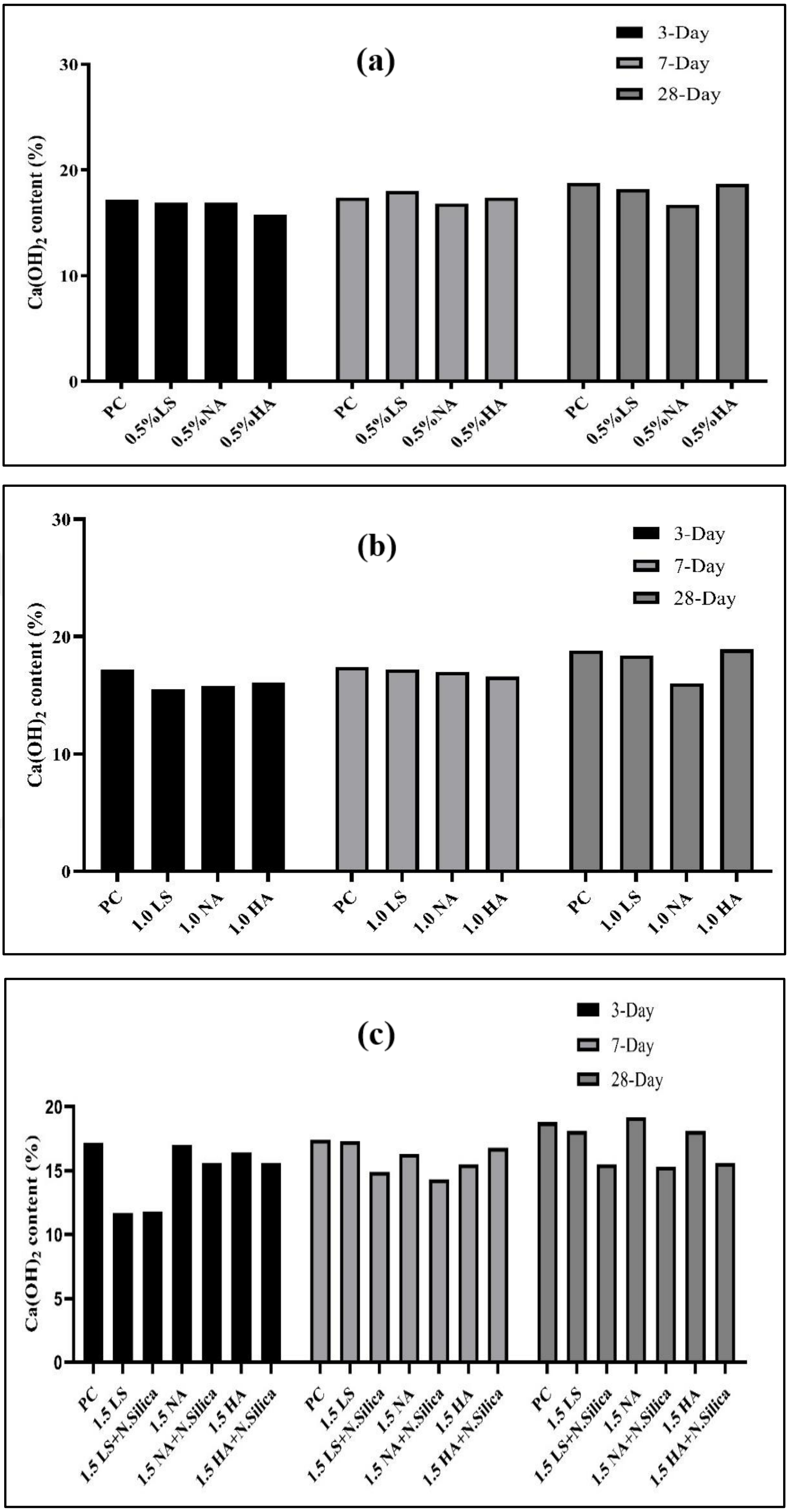


Figure 4.2.1 Ca(OH)$_2$ content of samples (a) represents 0.5% dosage (b) 1.0% and (c) 1.5% dosage.

Since the use of 0.5% dosage does not retardation effect on the hydration process, free $Ca(OH)_2$ content are very close to the control sample (Figure 4.2.1(a)).

At 1.0% dosage, because of the retardation of the hydration, free $Ca(OH)_2$ was reduced as seen in Figure 4.2.1(a). The hydration retardation effect of the LS-based sample is higher than the others, so free $Ca(OH)_2$ content is low at 3 days. This situation can be seen at 3 days, but at 7 and 28 days the effect finish as shown in Figure 4.2.1(a), Figure 4.2.1(b), Figure 4.2.1(c). At 1.0% and 1.5% dosage of free $Ca(OH)_2$ content of the NA-based sample seemed to be lower than the others at 28 days due to formation of hydration shell.

As shown in Figure 4.2.1(c), Due to pozzolanic reaction begins later, adding nano silica to the mixes with different types of superplasticizers cause decrease of the $Ca(OH)_2$ content at all dosages and days.

4.3. Flow Table Experiment

After casting mortar samples, workability test was carried out by using the flow table in accordance with ASTM C230M - 14 standard.

Figure 4.3.1 shows the results of the experiment. At a dosage of 0.5%, the flow values have the largest value of the LS-based sample and the others are NA and HA-based samples, respectively. In this dosage, NA and HA-based admixtures did not provide an effective flow value on cement mortars.

At a dosage of 1.0%, the flow values of the admixtures used are the closest to each other. The purpose of this study is to illustrate the ability of humic acid to make the same effect as the superplasticizers used today.

At a dosage of 1.5%and 1.0%, the flow values of the HA and LS-based samples were approximately equal to each other. However, the NA-based sample showed a slight increase. It is understood that; increasing the dosage from 1.0% to 1.5% does not give extra workability for HA and LS-based samples but, for NA-based sample cause certain flow value and this increasing may be significant depending on the field of use.

In addition, the use of 5.0% nano silica in the cement mixture had no significant effect on the workability values.

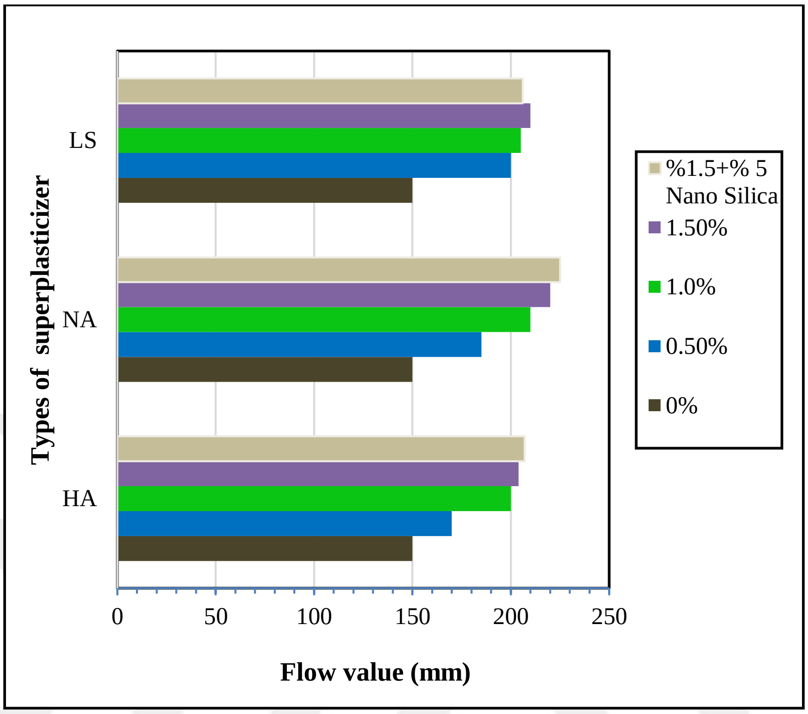


Figure 4.3.1 Flow values of fresh mortars

4.4. Setting Time

HA and NA-based samples behave closely to each other at each dosing, while the setting time values of LS-based sample are far from these values.

Even at this lowest dosage, there is a difference of about 7 hours between the initial setting time value of the LS-based sample and the initial setting time value of the control sample. At a dosage of 0.5%, the HA-based sample to the control sample increased the initial setting value by 6 minutes, while the NA-based sample increased 71 minutes. The final setting value of the HA-based sample is 100 minutes longer than the NA-based sample.

At a dosage of 1.0%; the initial setting value of 240 minutes for the HA-based sample and 307 minutes for the NA-based sample was observed. In their final setting time values, 84 minutes delay was observed in HA-based material. As observed, the HA-based sample at a dosage of 1.0% shows similar results with the NA-based sample in the setting time experiment. At a dosage of 1.5%, the difference between the initial setting and the final setting increases. The use of nano silica in this dosage, the initial and final setting time values decreased slightly due to the increased surface area and increasing the water requirement. The use of this dosage for LS-based samples may cause problems about demolding time.

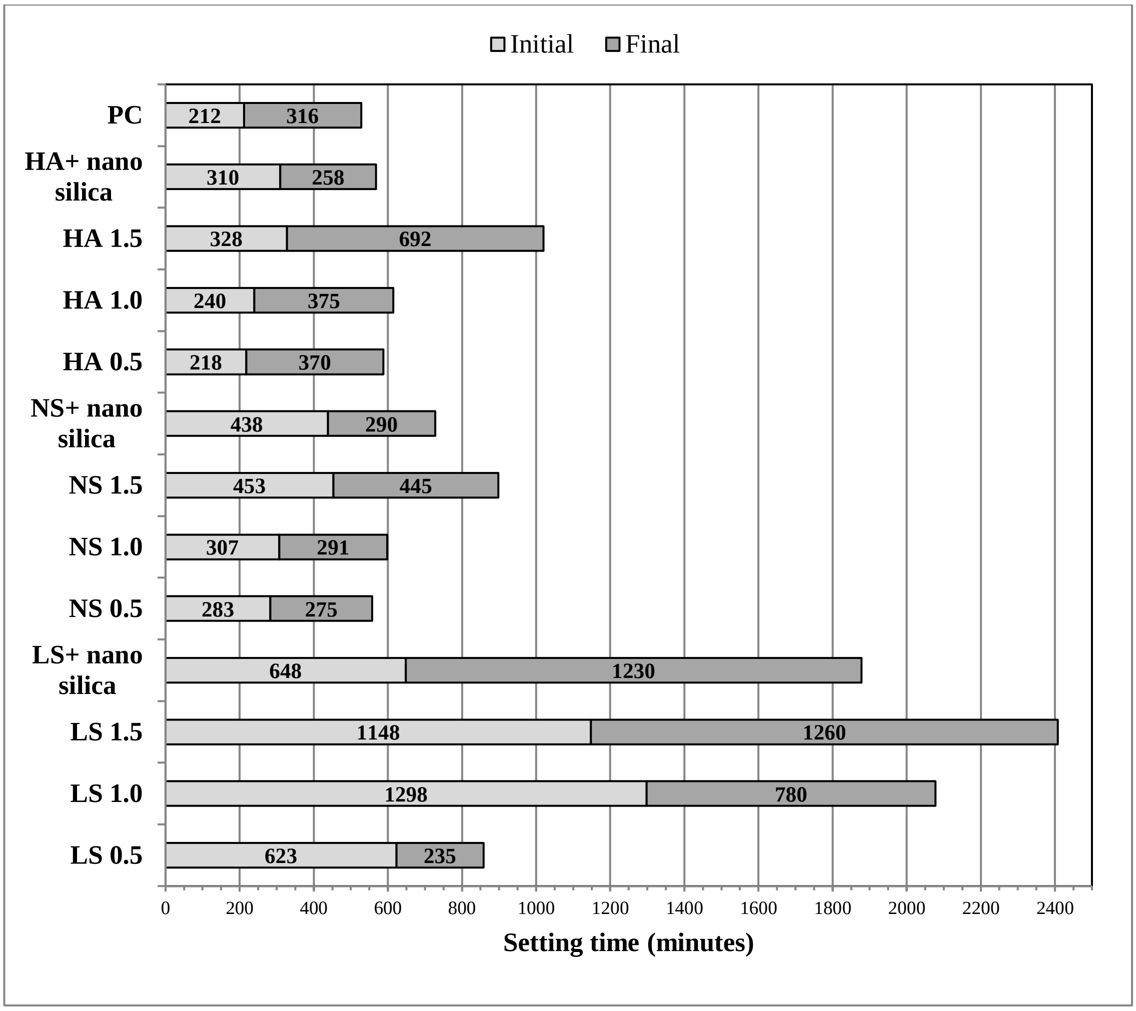


Figure 4.4.1 Values of initial and final setting time

4.5. Compressive Strength

Compressive strength values of the cement mortars with different admixtures at 3,7,28 day of age is shown in Table 4.5.1. Also, Figure 4.5.1 was prepared in order to see the changes of the samples depending on dosages and days between each other more easily.

Table 4.5.1 Compressive strength of mortars

Cement Sample	3-day (MPa)	7-day (MPa)	28-day (MPa)
PC	25.5	36.1	46.5
PC+ 0.5%LS	29.8	44.3	51.4
PC+ 1.0%LS	29.7	45.7	49.9
PC+ 1.5%LS	30.9	40.7	41.3
PC+%5 NanoSilica+1.5%LS	26.9	37.9	46.6
PC+ 0.5%NA	31.9	40.4	42.5
PC+ 1.0%NA	32.9	35.4	43.6
PC+ 1.5%NA	28.4	34	43.9
PC+%5 NanoSilica+1.5%NA	32.4	38.3	48.8
PC+ 0.5%HA	29.6	43.2	48.3
PC+ 1.0%HA	30.0	39.2	47.0
PC+ 1.5%HA	29.3	37.0	47.2
PC+%5 NanoSilica+1.5%HA	27.2	35.9	43.0

At a dosage of 0.5%, at 3 days of the compressive strength values of LS, NA, HA-based samples were significantly higher than the value of the control sample. The values of LS and NA-based samples are 17% higher than the control sample, while the NA-based sample is 25% higher (Table 4.5.1 and Figure 4.5.1(a)).

At 7 day, the compressive strength value of the NA-based sample was lower than the compressive strength values of the LS and HA-based samples as shown in Table 4.5.1

and Figure 4.5.1(a). The reason for this behaviour is that the NA-based sample causes irregular hydration shell formation due to the hydration rate at 3 days.

According to Galluccini hydration shell continues to form up to 3 days, but at the end of the third day reaches a considerable thickness. The rate of formation of this heterogeneously growing shell causes some mechanical defects [78]. Although this process was delayed by the use of superplasticizers, this study showed itself at 7 days.

At 28 of age, due to the reduced hydration rate of the NA-based sample, it did not reach strength value of others sample. However, LS and HA-based samples showed a more regular increase (Table 4.5.1 and Figure 4.5.1(a)). At a dosage of 1.0%, the percent increase in compressive strength of LS, NA, and HA-based samples compared to the control sample for 3 days was 17%, 30% and 18%, respectively. Similar behaviour was observed with the behaviour at dosage of 0.5%. hydration shell formation also left the NA-based sample behind the other samples at 7 and 28 days as shown in Table 4.5.1 and Figure 4.5.1(b).

At a dosage of 1.5%; compressive strength values at 3 days of all samples are close to each other and about 15% higher than the control sample. At 7 days, while the LS and HA- based samples were able to sustain the development of compressive strength, the NA-based sample was left behind. At 28 days, the NA and LS-based samples have lower values than the control sample, whereas the HA-based sample was the only sample that could exceed the compressive strength of the control sample (Table 4.5.1 and Figure 4.5.1(c)).

The use of nano silica at a dosage of 1.5% caused an increase of the compressive strength value at NA and LS-based samples, whereas HA-based sample did not show compatibility with nano silica as seen in Table 4.5.1 and Figure 4.5.1(c).

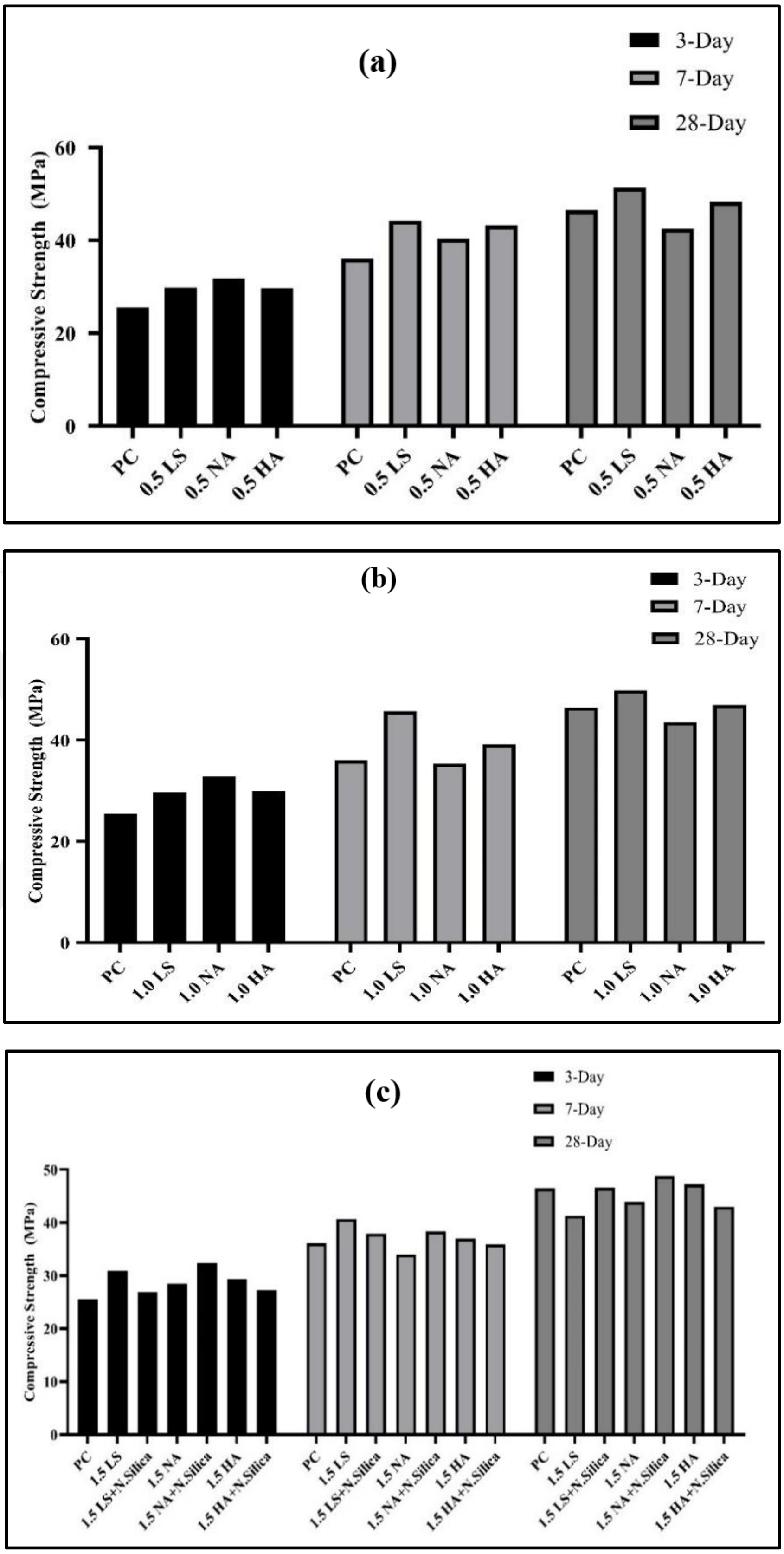


Figure 4.5.1 Compressive Strength of samples (a) represents 0.5% dosage (b) 1.0% and (c) 1.5% dosage.

Chapter 5

Conclusions and Future Prospects

5.1. Conclusions

In this study, the commercially available humic acid (HA)-based solution, obtained from leonardite, investigate the plasticizing efficiency comparatively with respect to lignin based (LS) and naphthalene-based (NA) superplasticizers in cementitious systems. Three different admixtures (LS, NA, HA-based) are used at three different dosages (0.5%, 1.0% and 1.5%) in cement mixtures. In order to observe the effect of humic acid on pozzolanic reaction, 5.0% nano silica was added to only 1.5% dosage of HA-based samples. For comparative evaluation, 5.0% nano silica was also added to other 1.5% dosage of LS, NA, HA-based samples. By evaluating the experimental results of this study, the following conclusions can be drawn;

1. In the chemical composition of the powder form NA, LS and HA solution, the amount of K_2O of HA-based solution was observed to be high. However, when the total amount of alkali was calculated, it was observed that the NA-based sample have a similar alkali content with the HA-based sample.

2. As a result of the isothermal calorimeter experiments, in the heat flow graphs of the cement paste with HA-based and NA-based solutions showed similar behaviours, but the LS-based sample was different from them at every dosage. Furthermore, using nano silica in cement mixture causes a decrease in the initial hydration peak. But, according to the total heat of hydration graph, for 1.5% dosages of each admixture material, using nano silica bring about an increase total hydration rate compared to mixtures which do not contain nano silica.

3. According to cement paste samples of the TGA results, at a dosage of 1.5%, a significant decrease in the at 3 days of $Ca(OH)_2$ content of the LS-based sample was observed. The at 3 days of $Ca(OH)_2$ content of NA and HA-based samples were close

to each other. The at 7 days of $Ca(OH)_2$ contents of LS, NA and HA-based samples show similar values according to their dosages. At 28 days, the $Ca(OH)_2$ content of the NS-based sample lagged behind the others. When using nano silica at a dosage of 1.5%, a decline in $Ca(OH)_2$ content is observed due to the pozzolanic reaction.

4. For the measured of workability, the flow table test was performed on cement mortars. The desired plasticizing efficiency was achieved at a dosage of 1.0%. Flow values at this dosage are similar for all plasticizers. Increasing the dosage from 1.0% to 1.5%, for HA, LS and NA-based admixtures do not cause a significant increase in the flow value. The use of 5.0% nano silica at a dosage of 1.5%, and did not bring about a significant change on flow values.

5. As a result of the setting time test, even at this lowest dosage, there is a difference of about 7 hours between the initial setting time value of the LS-based sample and the initial setting time value of the control sample. NA-based and LS-based samples showed close initial and final setting values at 0.5% and 1.0% dosages. However, the final setting value of the HA-based sample at 1.5% dosage was delayed by about 4 hours. The use of 5.0% nano silica at a dosage of 1.5%, cause a decrease in the initial and final settings of all dosages.

6. For the determination of mechanical property of hardened cement mortar samples, compressive strength test was performed at 3, 7, 28 days. The compressive strength values of HA-based samples are between the compressive strength values of LS and NA-based sample at 3 days and at 7 days. However, according to the 28-day compressive strength values, NA based samples lagged behind NS and HA. Using nano silica, compressive strength values of the NA-based sample increased at 3,7 and 28 days, but the compressive strength values of the HA-based sample decreased at 3,7 and 28 days. According to this result, it can be observed that humic acid and nano silica are not compatible.

The humic acid solution obtained from leonardite were evaluated comparatively with lignin-based (LS) and naphthalene-based (NA) solutions in cementitious systems. The HA-based admixture showed similar behaviour with other admixtures in terms of fluidizing activity. In addition, due to the effects of HA-based admixture on workability, hydration kinetics and mechanical properties in the cementitious system should be considered as eco-efficient superplasticizers.

5.2. Future Prospects

In this study, humic acid, which was dissolved in alkaline medium, was obtained commercially available. That is, the humic acid used in the experiments is potassium humate in the salt form. The repetition of these experiments should be carried out with pure humic acid in order to find out whether the alkali content or the amount of humic acid in the commercially available HA-based solution affects the workability performance.

Since humic acid is dissolved in alkali medium and added to the mixing water, alkaline silica reaction test should be performed in order to observe the expansion in a long time.

The incompatibility of the HA-based solution and the nano silica combination should be investigated whether it will continue in the use of pure humic acid. The compatibility of humic acid with other pozzolanic materials can be investigated and the most effective pozzolan material can be determined. With the use of both natural raw material superplasticizer and pozzolan, the amount of cement can be reduced significantly and the reduction of CO_2 emission can be observed in the Life Cycle analysis.

Thus, an important contribution will be made in the production of eco-efficient superplasticizers, based on domestic raw materials against the superplasticizers produced by imported raw material input and high energy consumption.

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APPENDIX

TGA PLOTS FOR CEMENT PASTE WITH AND WITHOUT SUPERPLASTICIZER

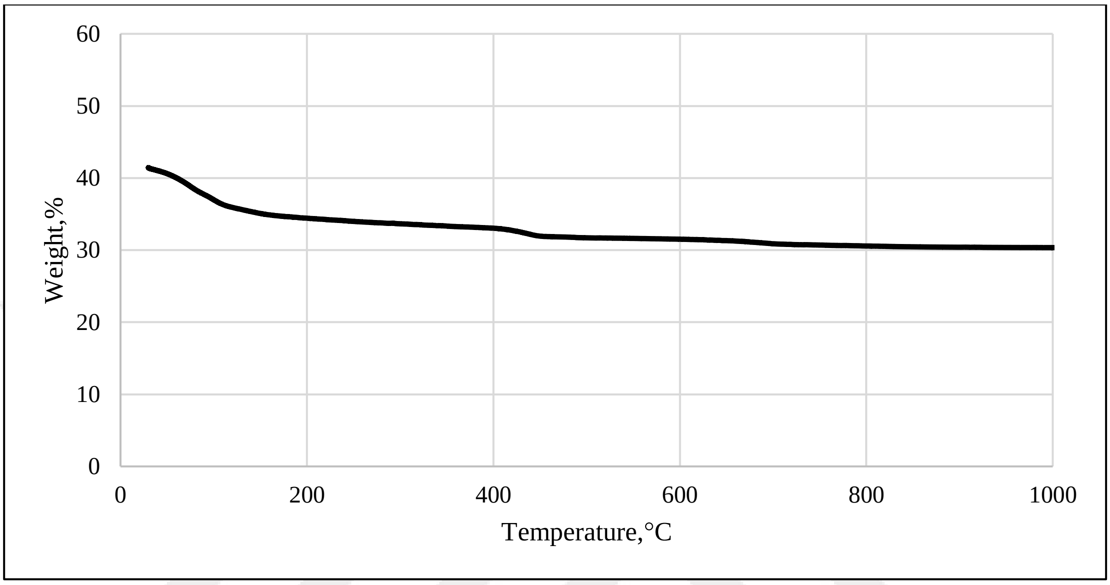


Figure A.1 TGA plot of Portland Cement paste at 3 days

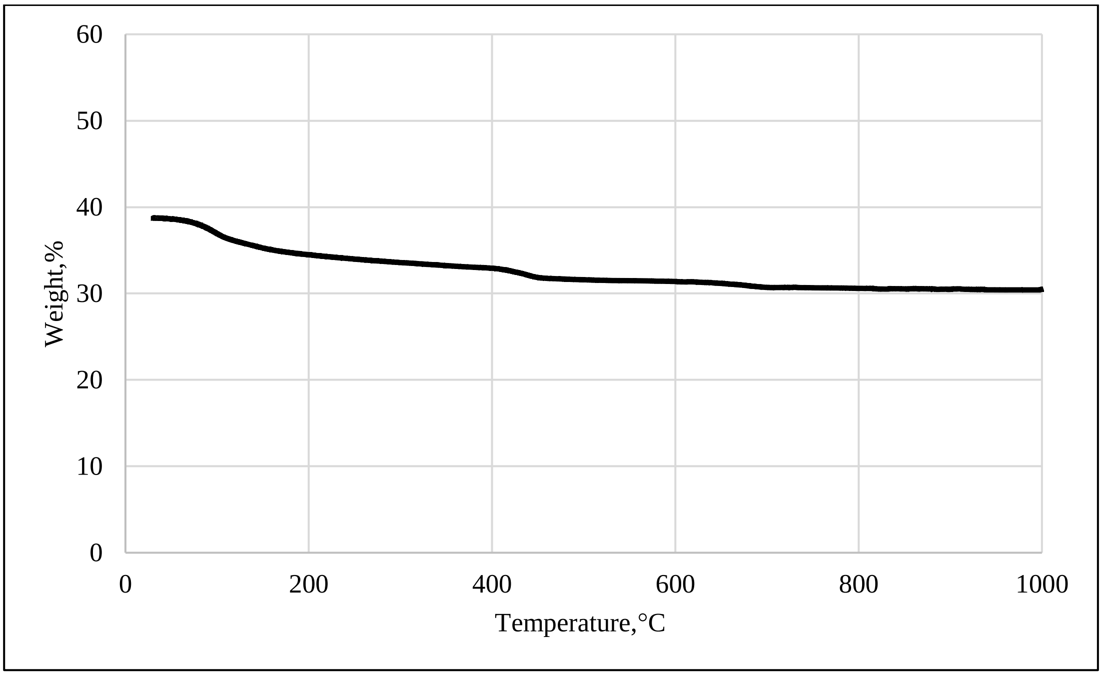


Figure A.2 TGA plot of Portland Cement paste at 7 days

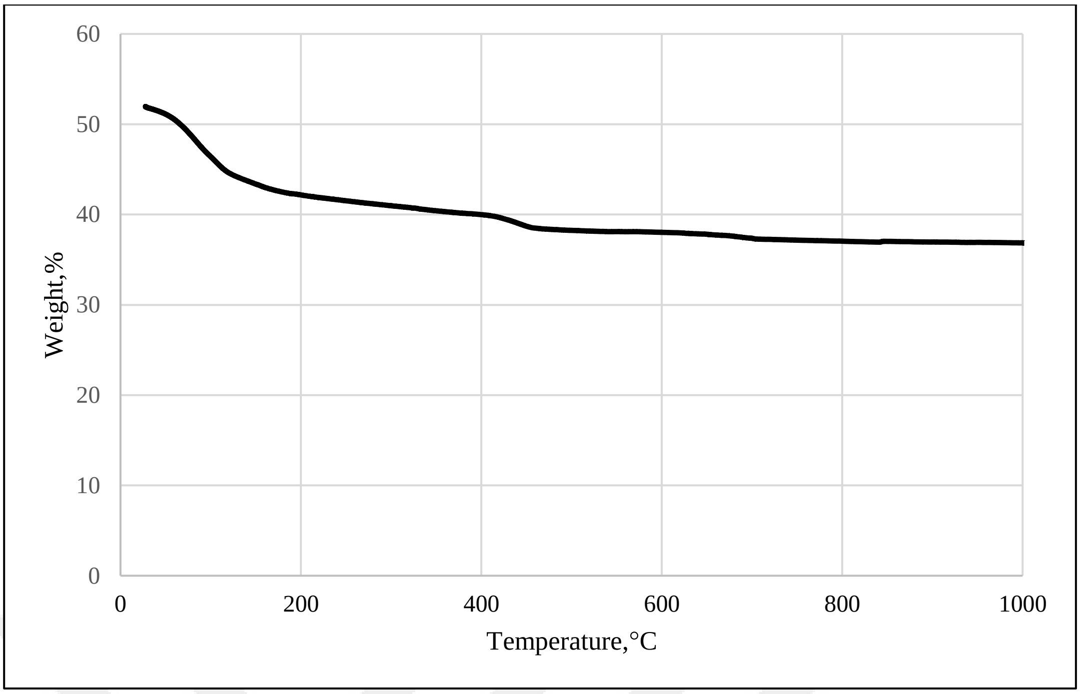


Figure A.3 TGA plot of Portland Cement paste at 28 days

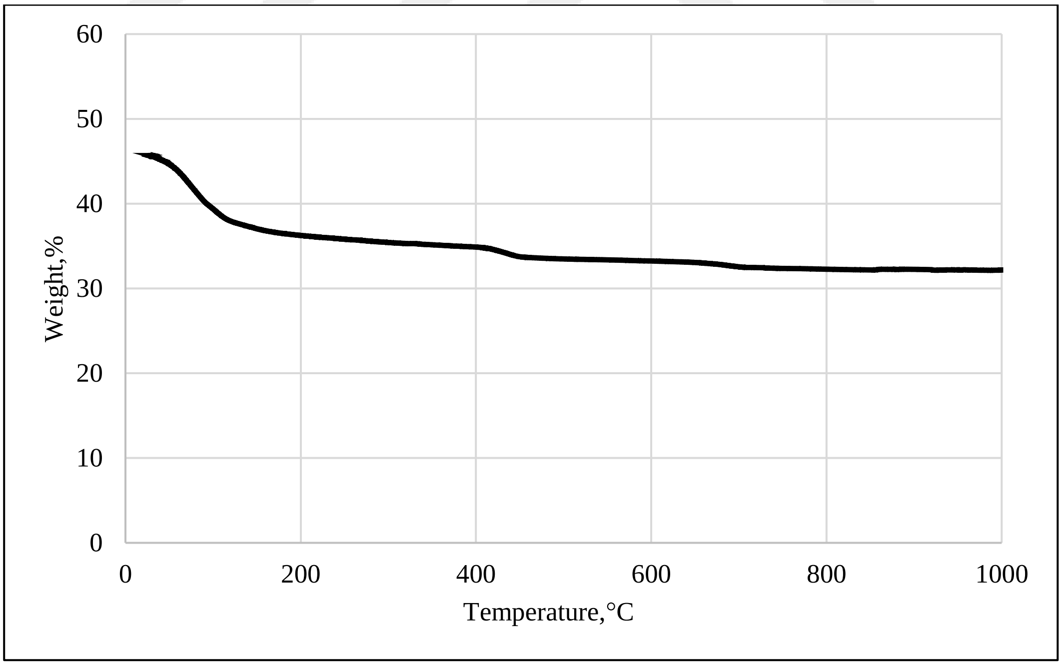


Figure A.4 TGA plot of cement paste with 0.5% LS at 3 days

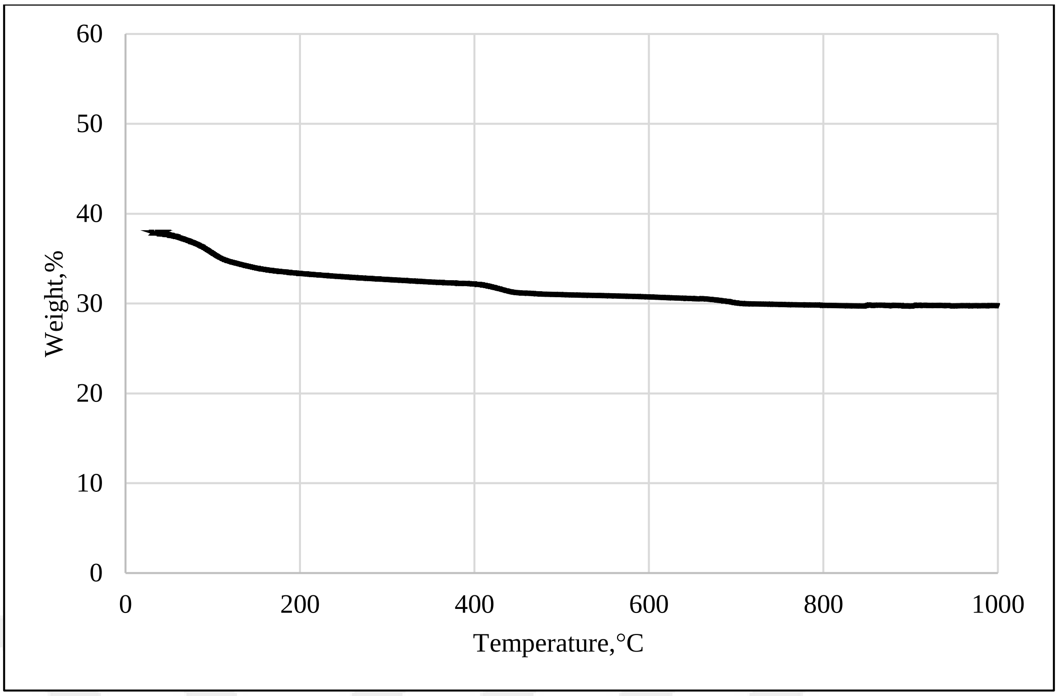


Figure A.5 TGA plot of cement paste with 1.0% LS at 3 days

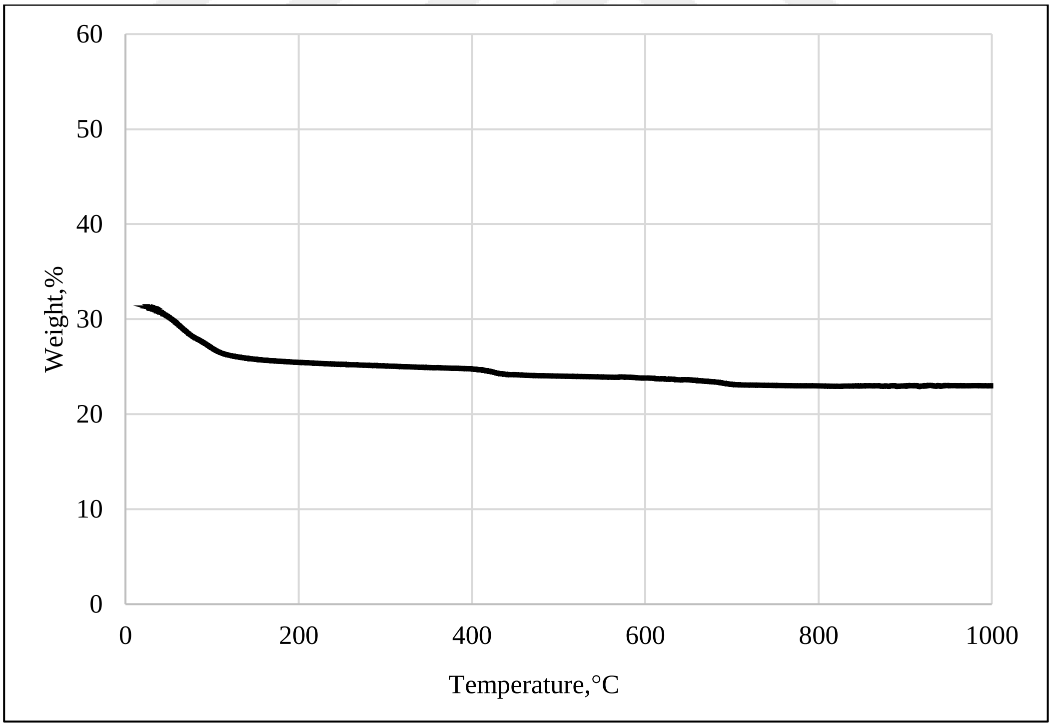


Figure A.6 TGA plot of cement paste with 1.5% LS at 3 days

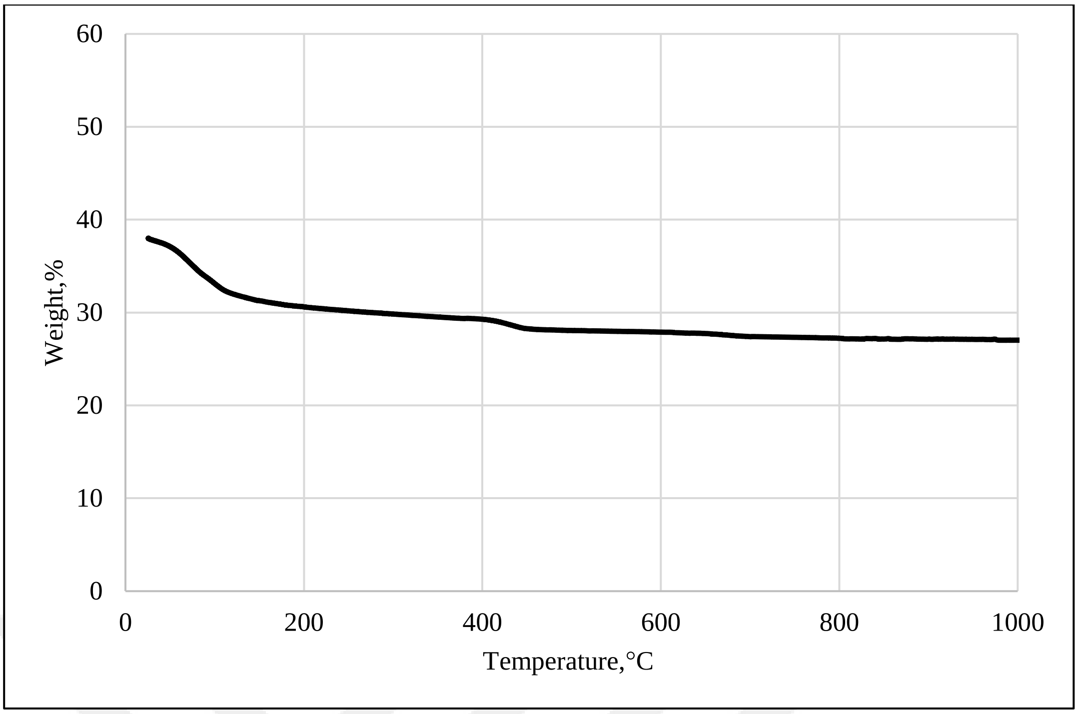


Figure A.7 TGA plot of cement paste with 0.5% LS at 7 days

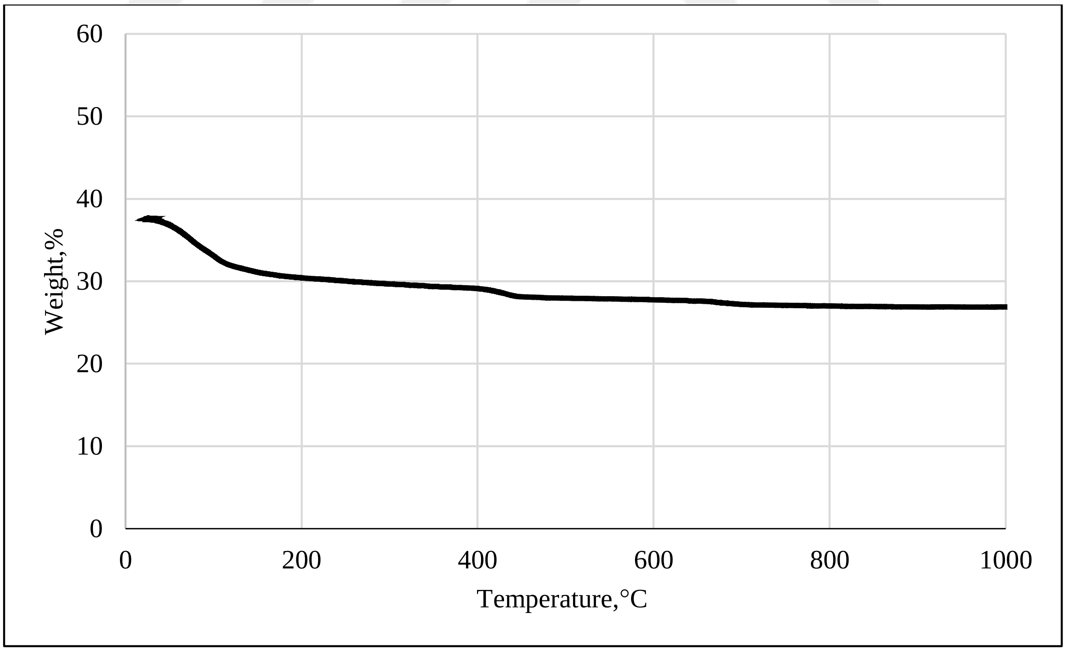


Figure A.8 TGA plot of cement paste with 1.0% LS at 7 days

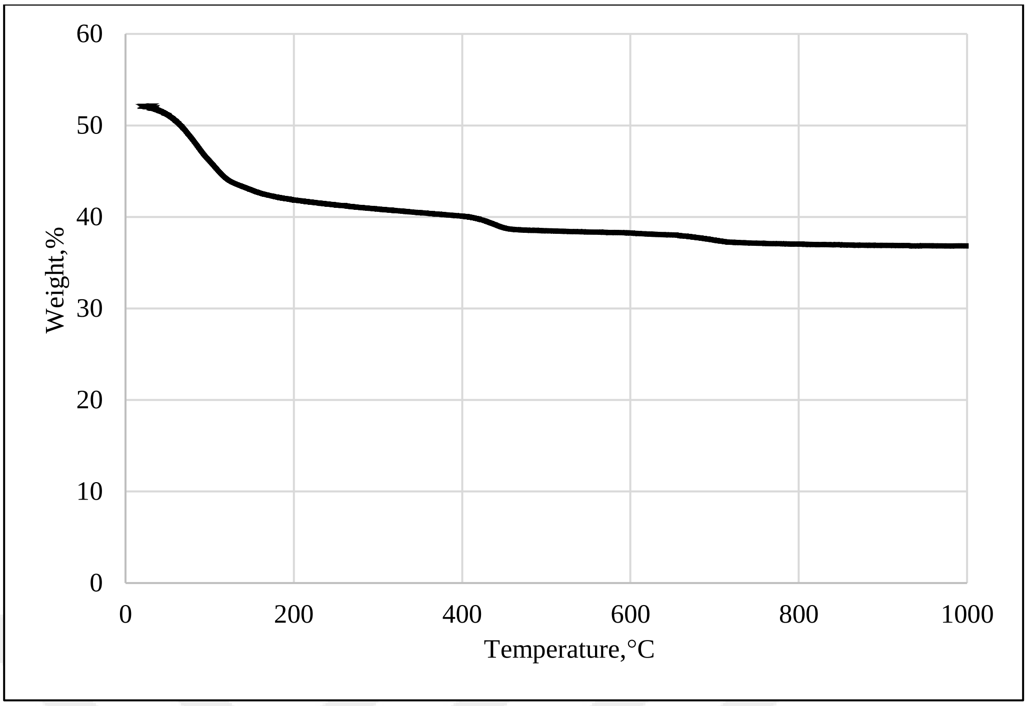


Figure A.9 TGA plot of cement paste with 1.5% LS at 7 days

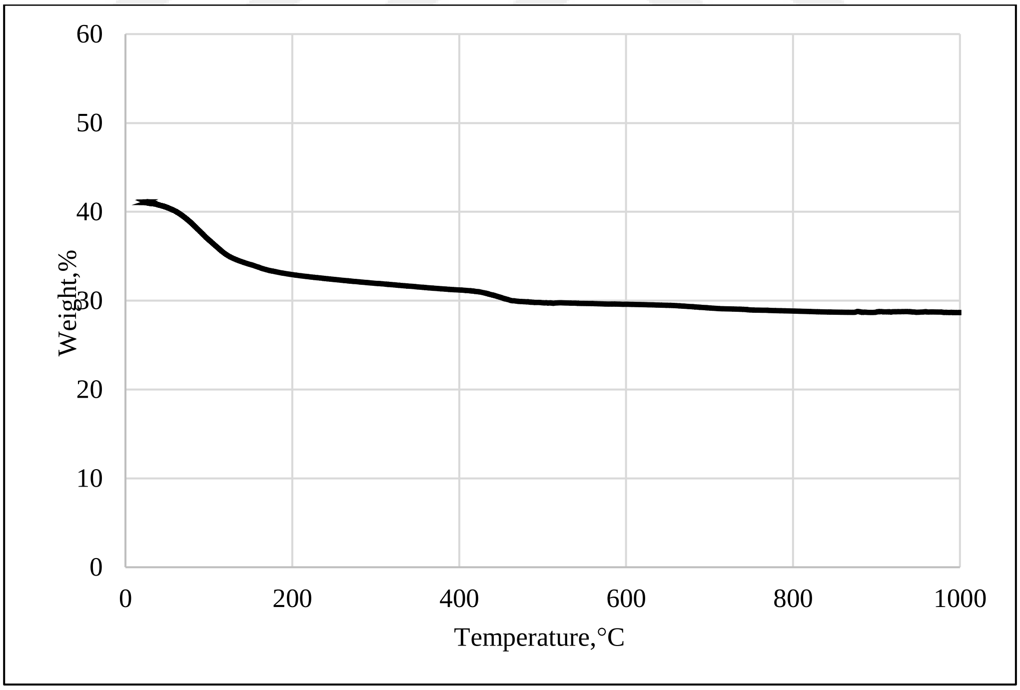


Figure A.10 TGA plot of cement paste with 0.5% LS at 28 days

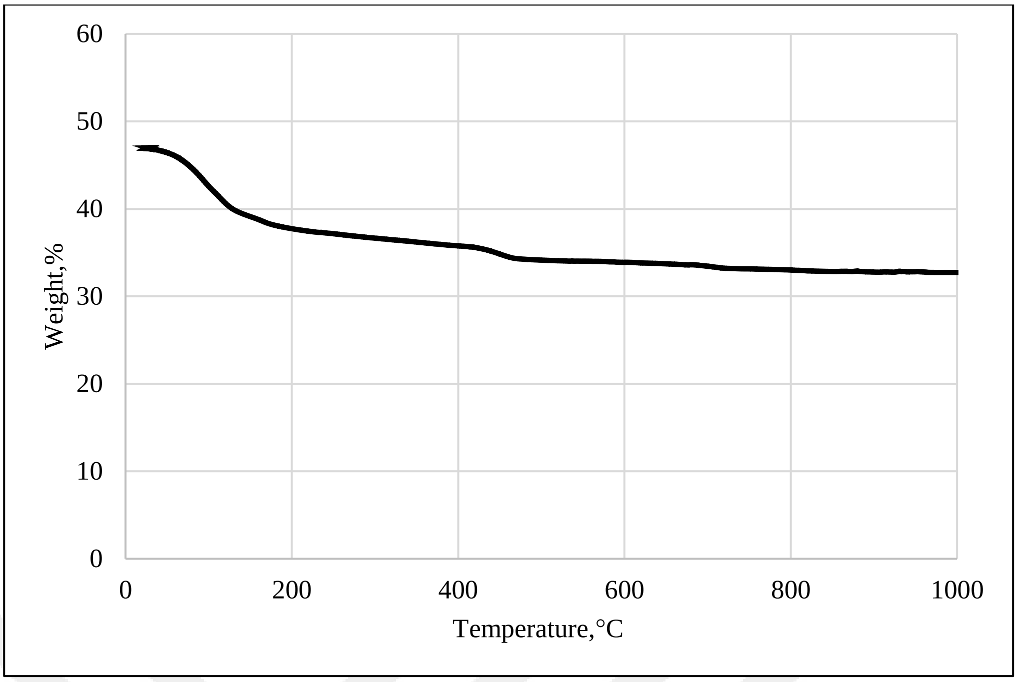


Figure A.11 TGA plot of cement paste with 1.0% LS at 28 days

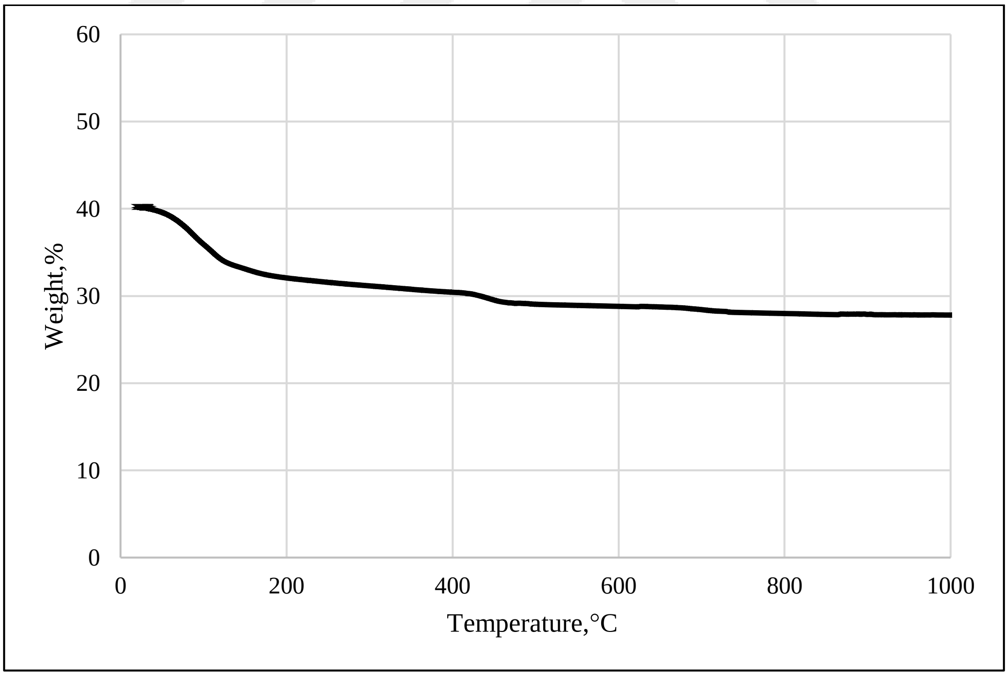


Figure A.12 TGA plot of cement paste with 1.5% LS at 28 days

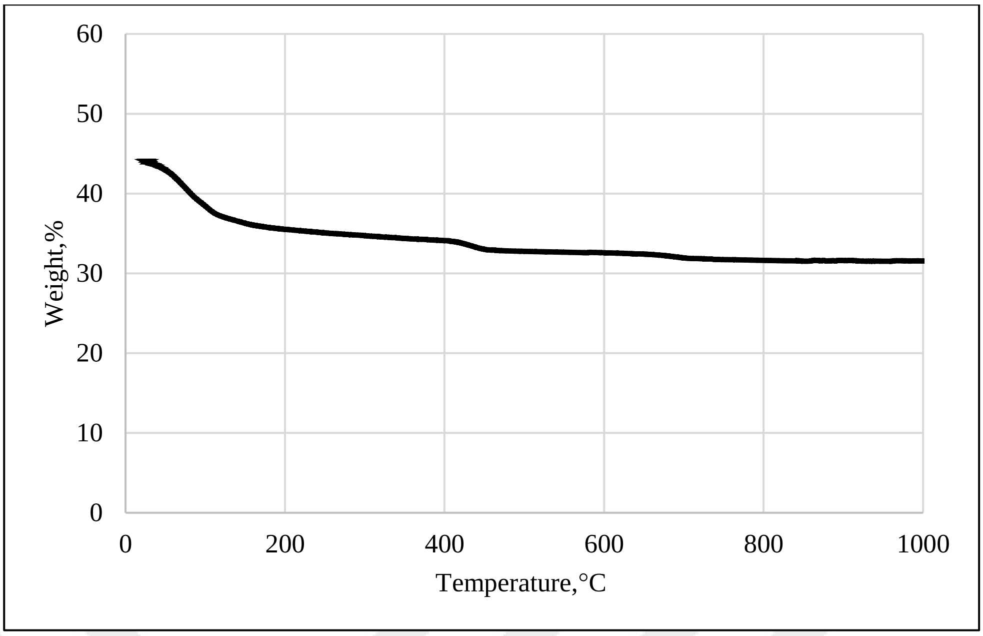


Figure A.13 TGA plot of cement paste with 0.5% NA at 3 days

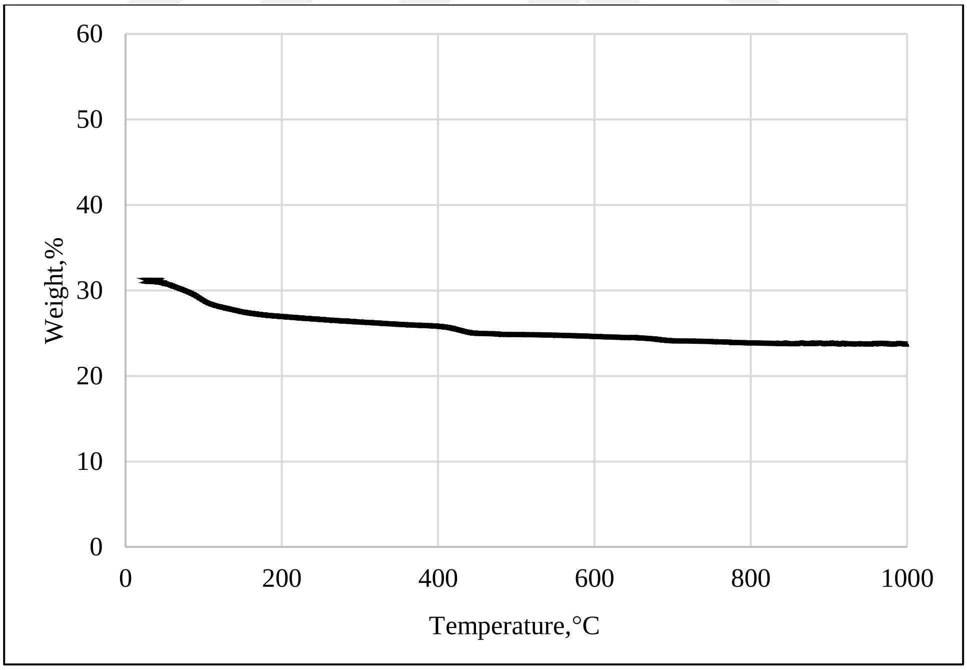


Figure A.14 TGA plot of cement paste with 1.0% NA at 3 days

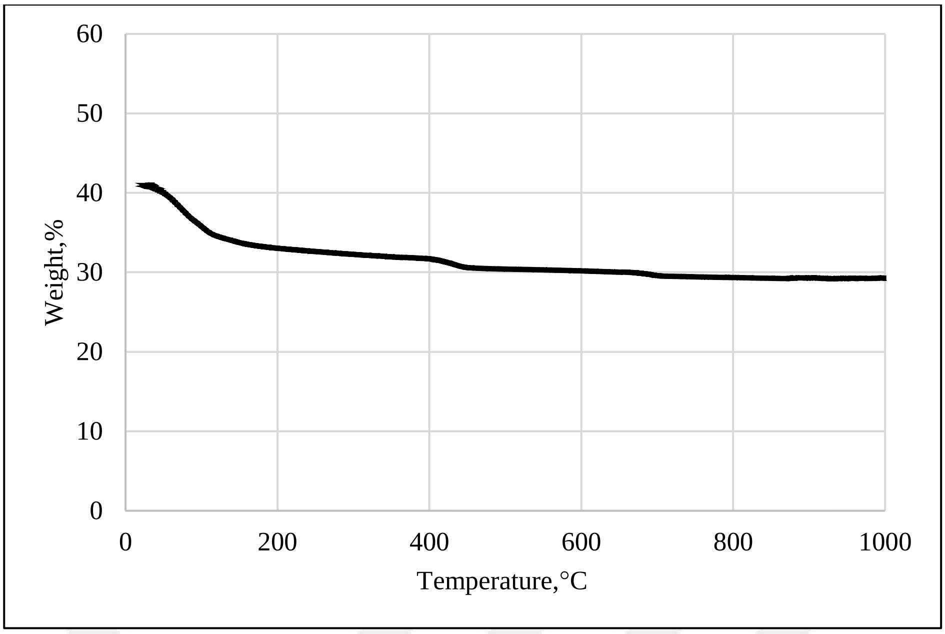


Figure A.15 TGA plot of cement paste with 1.5% NA at 3 days

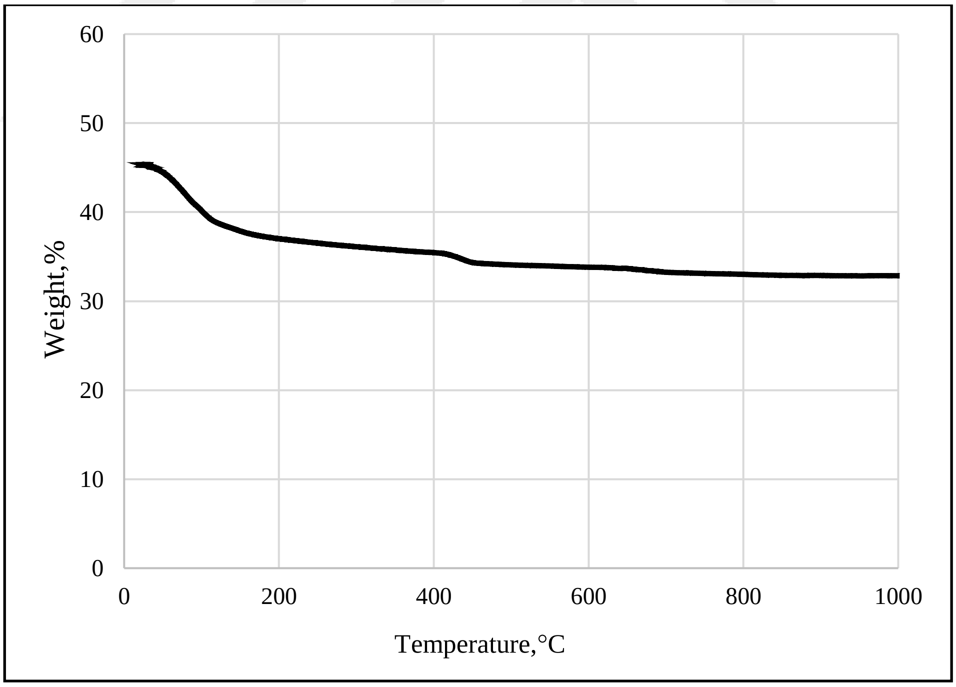


Figure A.16 TGA plot of cement paste with 0.5% NA at 7 days

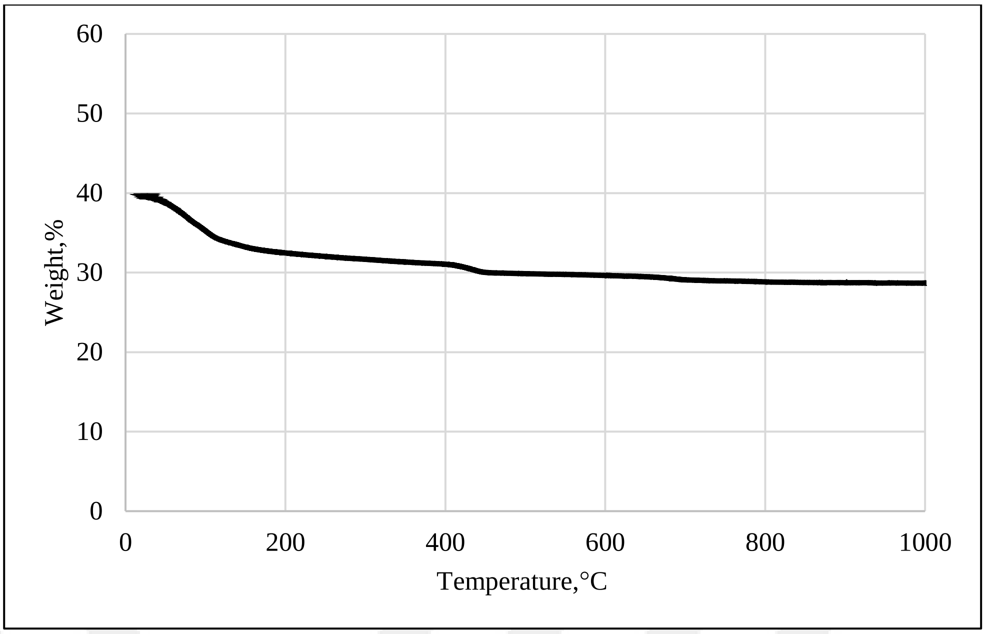


Figure A.17 TGA plot of cement paste with 1.0% NA at 7 days

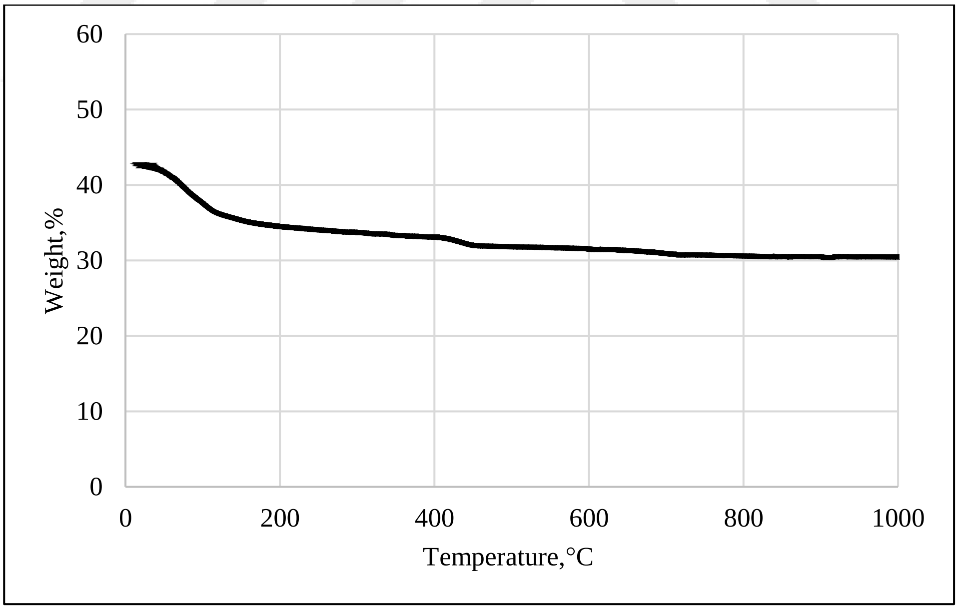


Figure A.18 TGA plot of cement paste with 1.5% NA at 7 days

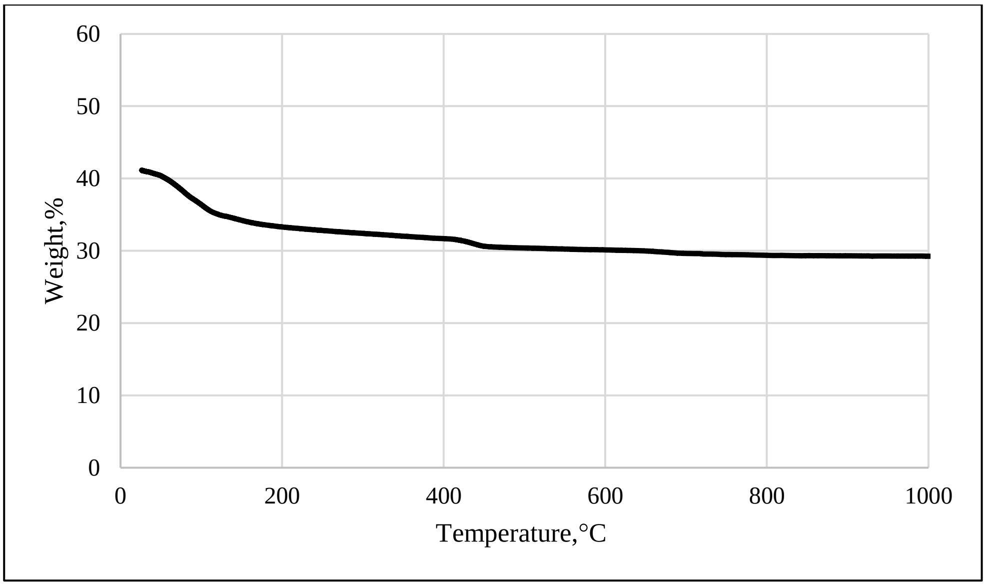


Figure A.19 TGA plot of cement paste with 0.5% NA at 28 days

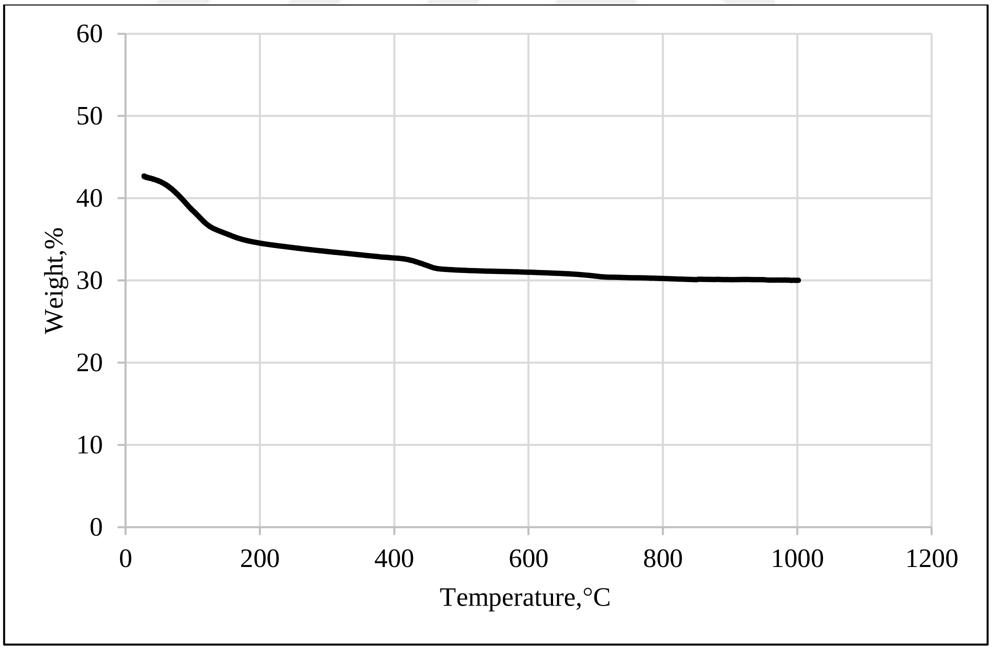


Figure A.20 TGA plot of cement paste with 1.0% NA at 28 days

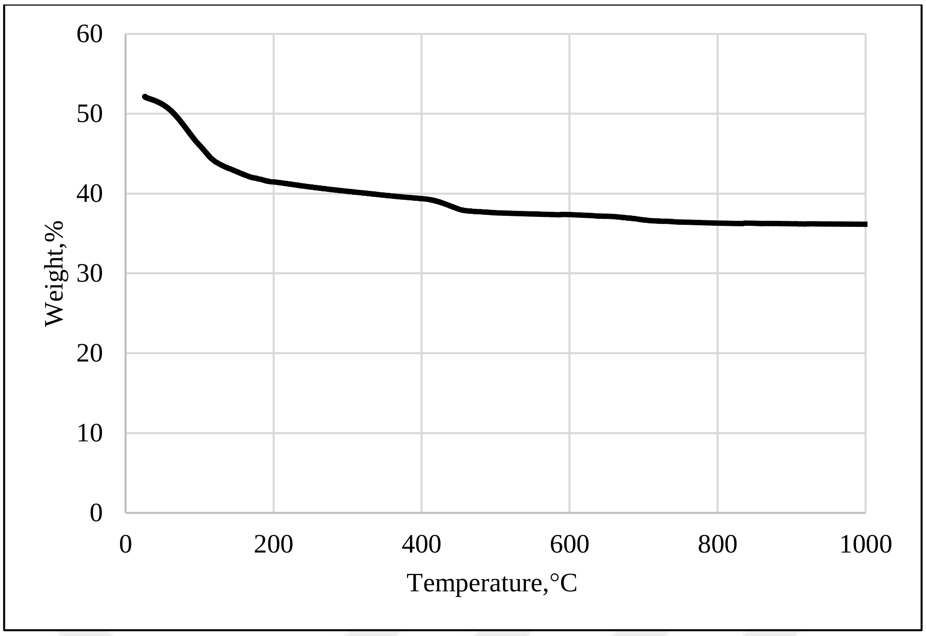


Figure A.21 TGA plot of cement paste with 1.5% NA at 28 days

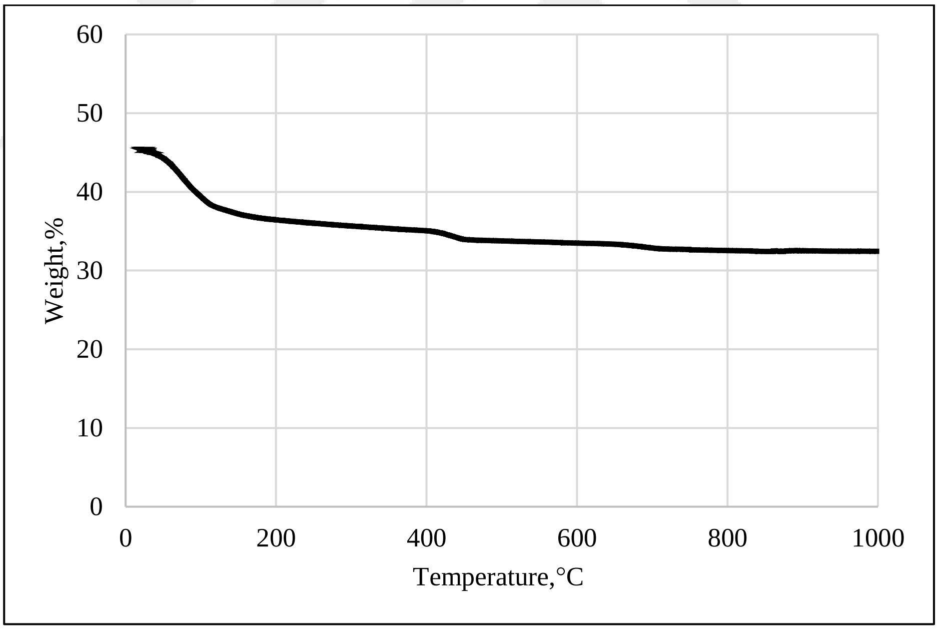
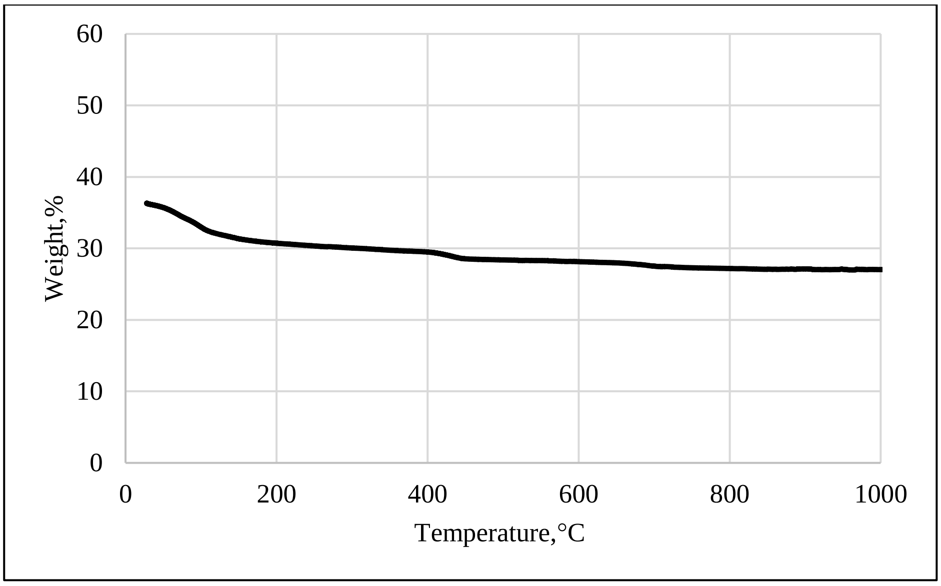


Figure A.22 TGA plot of cement paste with 0.5% HA at 3 days



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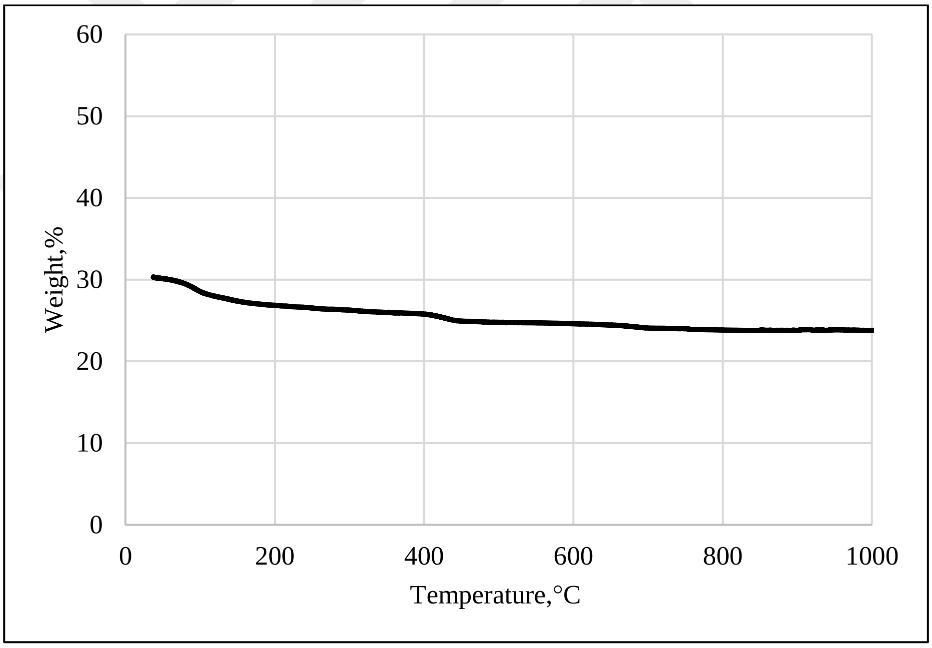

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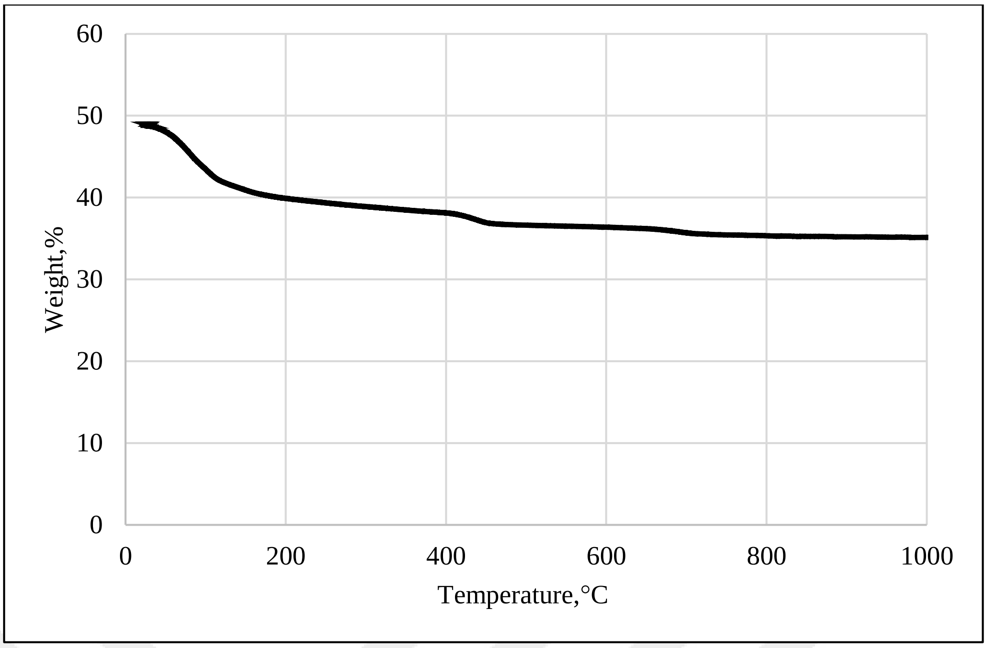

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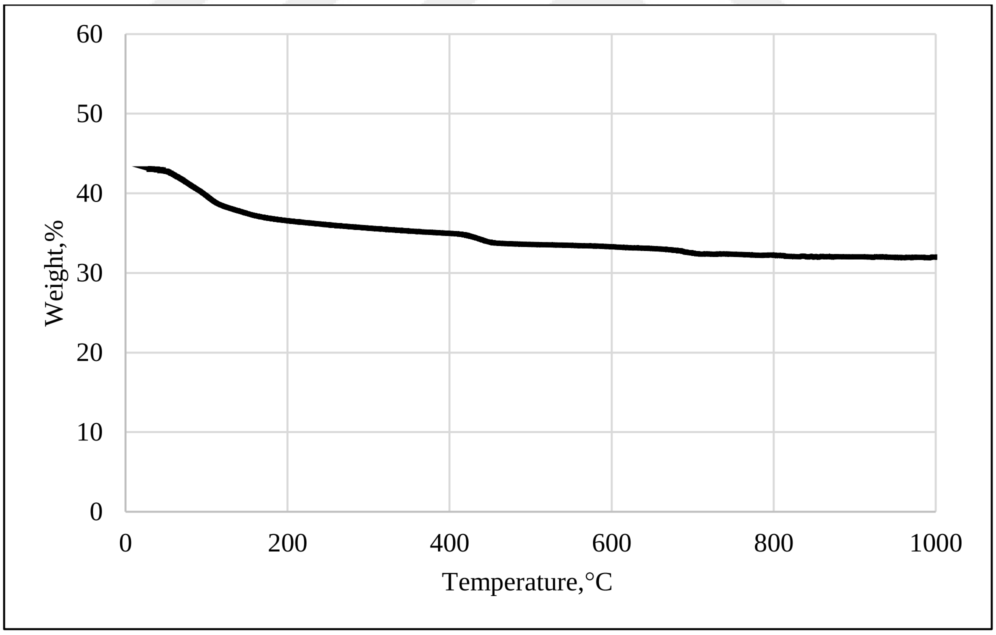

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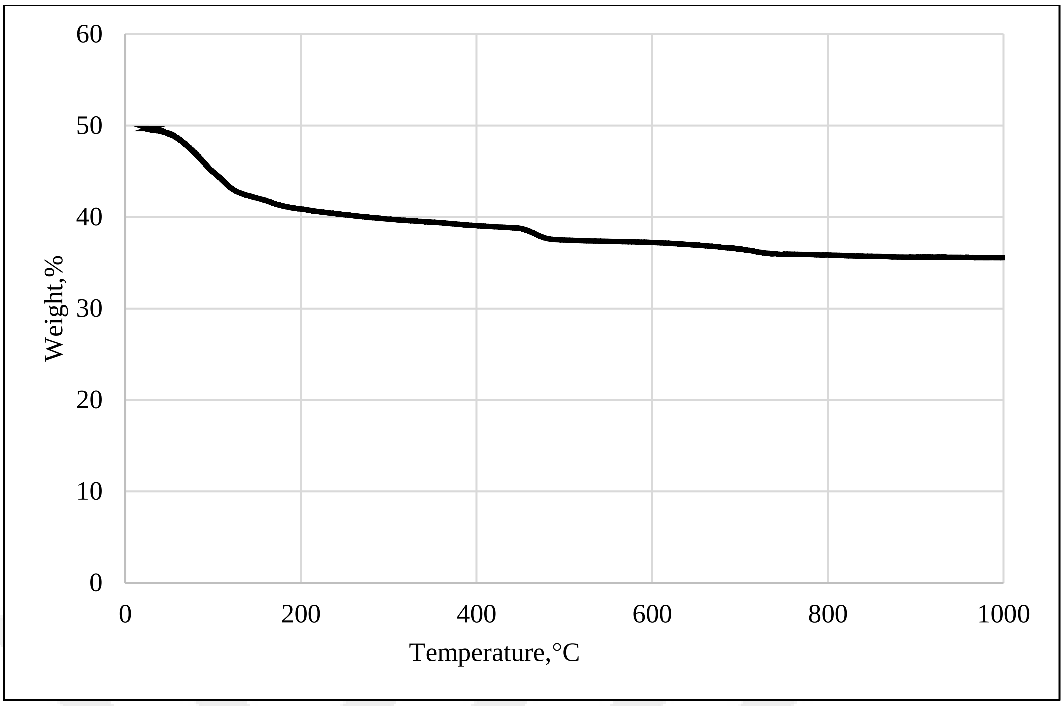

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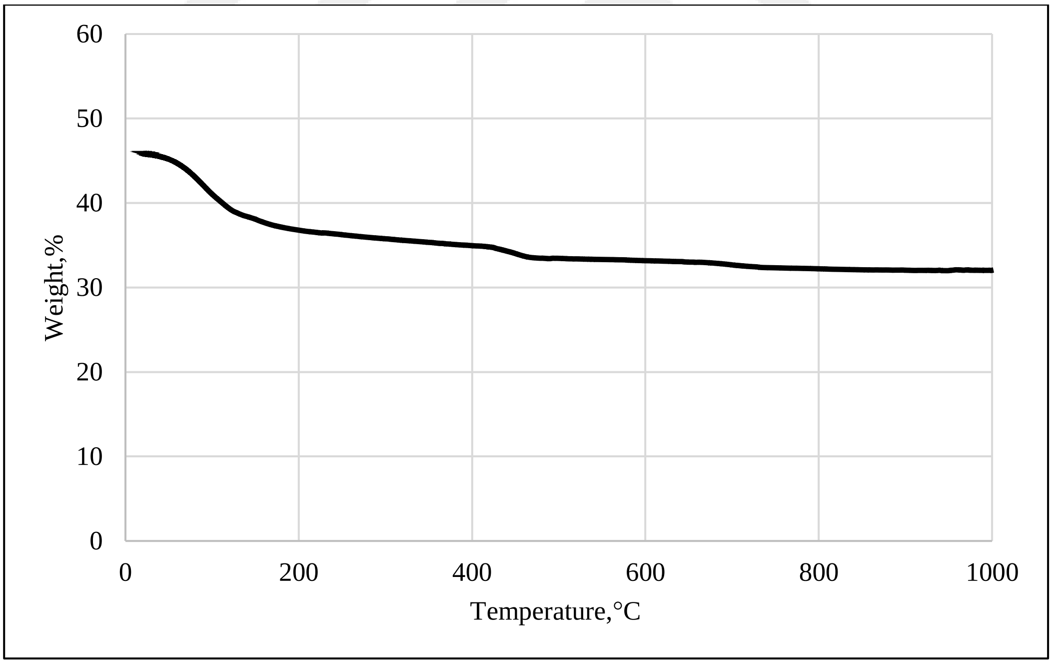

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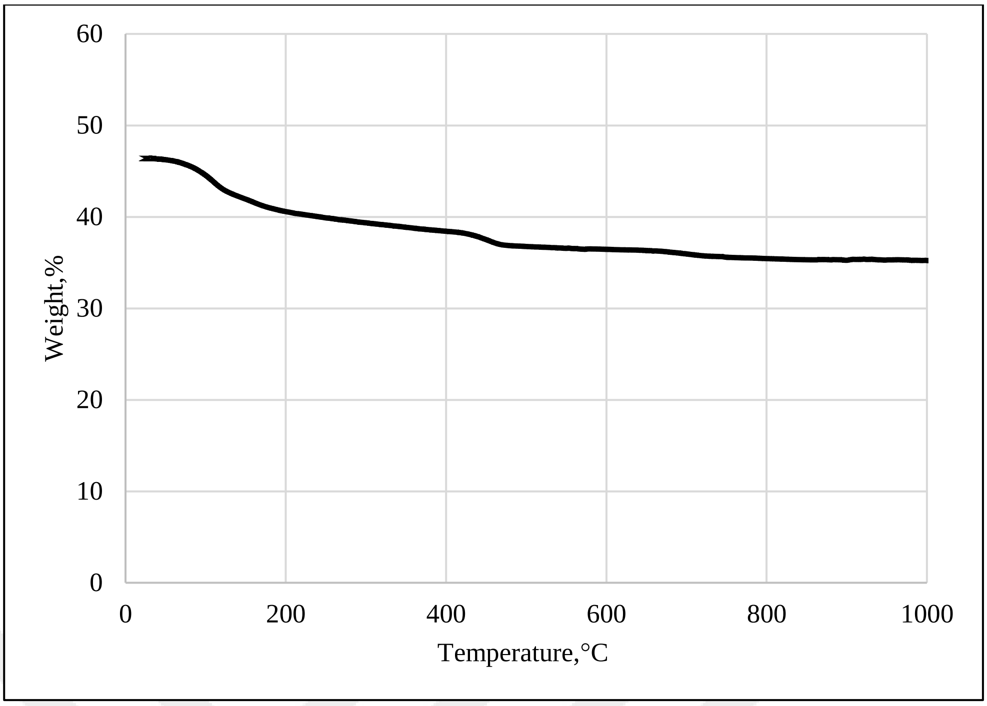

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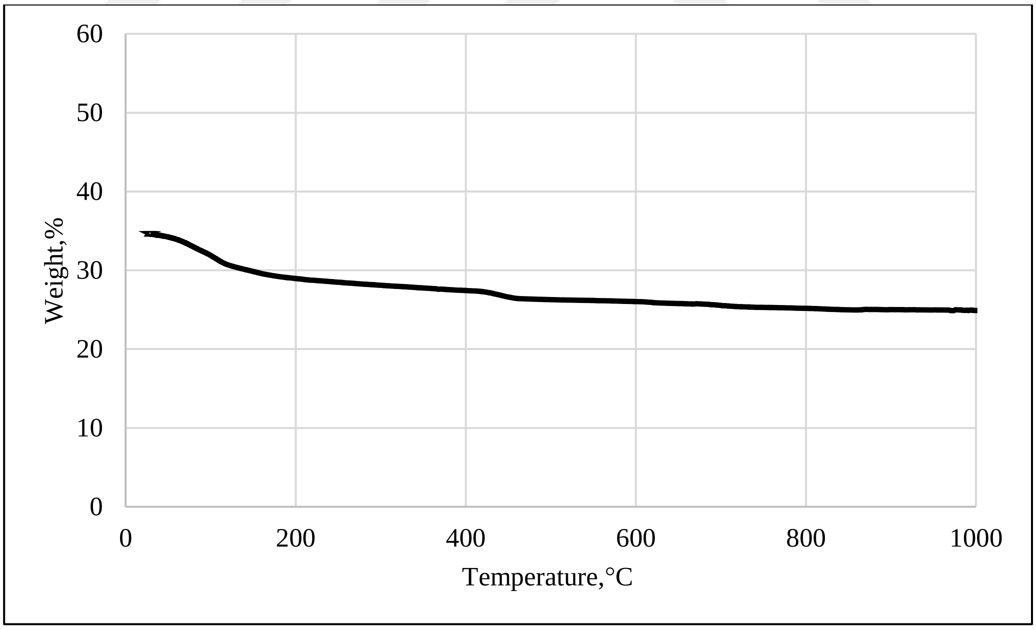

Figure A.30 TGA plot of cement paste with 1.5% HA at 28 days