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INVESTIGATION OF EFFECT OF PSSS ON CALCIUM SULFATE CRYSTAL MORPHOLOGY AND SIZE DISTRIBUTION

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

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ABSTRACT

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Master of Science in Chemical Engineering

Advisor: Asst. Prof. Dr. Muhammed Bora AKIN

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The effect of PSSS (Poly(sodium 4-styrenesulfonate)) and the effect of reactants concentration on calcium sulfate crystallization depends on the specific conditions of the experiment. Studies have shown that PSSS and the reactants concentration can influence the morphology and size distribution of calcium sulfate crystals under certain conditions. Therefore, it is important to consider the specific experimental conditions and parameters when evaluating the effectiveness of PSSS and the reactants concentration on calcium sulfate crystallization. In this study, the effect of changing equal concentration of reactants (0.04 M, 0.05 M, 0.06 M, 0.07 M and 0.08 M), on the formation of calcium sulfate ($CaSO_4$) crystals from the reaction of calcium chloride ($CaCl_2$) with sodium sulfate (Na_2SO_4) was investigated by using different concentrations of reacting compounds. The effect of PSSS as an additive and at different concentrations was also examined when the reactant concentration was kept constant at 0.04 M, and the additive used 0.001 g/L, 0.0025 g/L, 0.005 g/L, 0.010 g/L, 0.050 g/L, 0.1 g/L, 0.15 g/L and 0.250 g/L. XRD, SEM and BET analyses of the reaction products were used to investigate the effect of the varying concentrations on the crystals obtained at the end of the reaction. Although a change in crystal size was determined with increasing reactant concentration, change in crystal morphology was not observed.

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Keywords: Calcium sulfate, Crystallization, Poly(sodium 4-styrene sulfonate), Additive

ÖZET

PSSS'NİN KALSİYUM SÜLFAT KRİSTAL MORFOLOJİSİ VE BOYUT DAĞILIMI ÜZERİNDEKİ ETKİSİNİN İNCELENMESİ

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PSSS'nin (Poli(sodyum 4-stiren sülfonat)) etkisi ve reaktan konsantrasyonunun kalsiyum sülfat kristalleşmesi üzerindeki etkisi, deneyin özel koşullarına bağlıdır. Çalışmalar, PSSS'nin belirli koşullar altında kalsiyum sülfat kristallerinin morfolojisini ve boyut dağılımını etkileyebileceğini göstermiştir. Bununla birlikte, çalışmalar, PSSS'nin kalsiyum sülfat kristalizasyonu üzerinde farklı etkilerini bildirmiştir. Bu nedenle, PSSS'nin kalsiyum sülfat kristalleşmesi üzerindeki etkinliğini değerlendirirken spesifik deneysel koşulları ve parametreleri dikkate almak önemlidir. Bu çalışmada, farklı konsantrasyonlarda reaksiyona giren bileşikler kullanılarak, reaktiflerin konsantrasyonunun değiştirilmesinin (Eşmolar 0,02 M; 0,03 M; 0,04 M; 0,05 M; 0,06 M; 0,07 M ve 0,08 M), kalsiyum klorürün ($CaCl_2$) sodyum sülfat (Na_2SO_4) ile reaksiyonundan kalsiyum sülfat ($CaSO_4$) kristallerinin oluşumu üzerindeki etkisi araştırıldı. Katkı maddesi olarak PSSS'nin etkisinin incelendiği deneylerde, reaktan konsantrasyonu 0,04 M'de sabit tutulmuş ve katkı maddesi 0,001 g/L; 0,0025 g/L; 0,005 g/L; 0,010 g/L; 0,050 g/L; 0,15 g/L ve 0,250 g/L kullanıldı. Reaksiyon ürünlerinin XRD, SEM ve BET analizleri konsantrasyonlarının reaksiyon sonunda elde edilen kristaller üzerindeki etkisini araştırmak için kullanıldı. Artan reaktan konsantrasyonu ile kristal boyutunda değişiklikler gözlenmesine rağmen, kristal morfolojisinde değişiklik gözlenmedi.

2023, 47 sayfa

Anahtar Kelimeler: Kalsiyum sülfat, Kristalizasyon, Poly(sodyum 4-stiren sulfonat), Katkı maddesi

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Ghassan Mutter Jassem JASSEM

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LIST OF SYMBOLS

°C	Degrees Celsius
g/L	Gram per liter
%	Percent
M	Molarity

LIST OF ABBREVIATIONS

ATMP	Aminotris(methylenephosphonic acid)
CSD	Crystal siz distribution
DMF	N, N Dimethylformamide
FE-SEM	Field Emission Scanning Electron Microscopy
FGD	Flue gas distribution
IPA	Isopropyl alcohol
OPC	Ordinary portland cement
PAA	Polyacrylic acid
pH	Power of hydrogen
PSA	Polystyrene sulfonic acid
PSSS	Poly(sodium-4-styrenesulfanate)
RO	Reverse osmosis
QCH	Micro-quartz system
SEM	Scaning electron microscopy
XRD	X- ray diffraction

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1. INTRODUCTION

Calcium sulfate is a chemical compound whose presence in nature is a white, solid, odorless powder. The water content of this material plays a key role in its presence in nature by the crystallization. Calcium sulfate is present in the form of anhydride ($CaSO_4$) if the crystallized does not contain water (Morikawa *et al.* 1975). In the form called bassanite and represented by the formula $CaSO_4.1/2H_2O$, each calcium sulfate molecule contains half a molecule of water (Taylor 1990). The calcium sulfate compound containing two molecules of water is the most common in nature and is called gypsum ($CaSO_4.2H_2O$) (Cole & Lancucki 1974). The reason for the difference in the properties of the calcium sulfate particles is due to the formation of crystals, the crystal structure and the amount of water they contain, as the particles that contain less water have more density, more hardness, and less solubility (M. V Thomas & Puleo 2009). As the increase in the amount of water entering into the composition of the particles means irregular crystals Which makes it leave interstitial capillary spaces between them, this means when the amount of water increases, the particles become less hard and more soluble (Kj 2003).

1.1 Calcium Sulfate

Calcium sulfate is a chemical compound that is commonly found in nature as the mineral gypsum. It has the chemical formula $CaSO_4$ and is composed of calcium ions (Ca^{2+}) and sulfate ions (SO_4^{2-}). Calcium sulfate is present in a wide variety of natural and synthetic materials. In its hydrated form, known as plaster of Paris, it is used in the construction industry as a building material, particularly for making walls and ceilings. It is also used as a dental casting material in dentistry. Calcium sulfate is also found in some types of food, such as tofu, which is often made with calcium sulfate as a coagulant. Additionally, it is sometimes added to foods as a nutritional supplement to increase calcium intake.

In industrial processes, calcium sulfate is used as a coagulant, afiller, and a fire retardant. It is also used in the manufacture of cement, as a soil amendment to improve the fertility of agricultural land, and in the production of paper and textiles. Overall, the presence of calcium sulfate in various materials and applications is due to its unique chemical and physical properties, which make it useful for a wide range of purposes.

1.2 Production of Calcium Sulfate

There are several methods for producing calcium sulfate, depending on the intended application and desired physical properties of the product. Some of the most common production methods include:

1. Extraction from natural sources,
2. Chemical reaction,
3. Byproduct from industrial processes,
4. Synthetic production.

1.2.1 Extraction from natural sources

Extraction from natural sources Extraction of calcium sulfate from natural sources typically involves mining deposits of gypsum rock, which is a soft mineral composed of hydrated calcium sulfate. The extraction process usually involves the crushing, grinding, calcination, grinding and packaging.

The raw gypsum rock is first crushed into smaller pieces using a crusher. This crushing step is necessary to make the raw material more manageable and to expose more surface area for subsequent processing. The crushed gypsum rock is then ground into a fine powder using a grinding mill. This grinding step helps to further break down the material and reduce its particle size. The ground gypsum powder is then heated in a rotary kiln or other type of furnace to remove the water of crystallization and convert it to anhydrous calcium sulfate, which is also known as "dead-burned" gypsum. The

temperature and duration of the calcination process depend on the desired properties of the final product. The calcined gypsum is then ground again into a fine powder and packaged for sale or further processing. In some cases, the gypsum may be milled into a different particle size or chemically treated to produce specialized products such as dental plaster or wallboard.

Overall, the extraction of calcium sulfate from natural sources is a relatively straightforward process that involves crushing, grinding, and calcination of the raw material. However, the quality and purity of the final product can vary depending on factors such as the quality of the raw material, the calcination conditions, and the grinding process.

1.2.2 Chemical reaction

The chemical reaction for the production of calcium sulfate from calcium carbonate and sulfuric acid can be represented by the following equation:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

In this reaction, calcium carbonate ($CaCO_3$) and sulfuric acid (H_2SO_4) are the reactants, and calcium sulfate ($CaSO_4$), carbon dioxide (CO_2), and water (H_2O) are the products.

The reaction proceeds as follows: the sulfuric acid reacts with the calcium carbonate to form calcium sulfate, carbon dioxide, and water. Calcium sulfate is produced in the form of dihydrate ($CaSO_4 \cdot 2H_2O$), which is a white, crystalline solid. The carbon dioxide and water are released as gases.

This reaction is exothermic, meaning that it releases heat as it proceeds. The reaction is typically carried out in a reactor vessel equipped with stirring and heating mechanisms. The reaction mixture is stirred to ensure uniform mixing of the reactants and to promote

the reaction. The temperature is typically controlled to optimize the reaction rate and product yield.

The resulting calcium sulfate product can be further processed and purified as needed for its intended application.

1.2.3 Byproduct from industrial processes

Calcium sulfate can be produced as a byproduct of various industrial processes, including the production of phosphoric acid, hydrofluoric acid, and titanium dioxide. The production of calcium sulfate as a byproduct typically involves the following steps:

Acid-base reaction: In the industrial process, an acid is reacted with a base to produce a salt and water. When calcium phosphate rock is used as a raw material for the production of phosphoric acid, gypsum is formed as a by-product of the phosphoric acid production process (B. Wang *et al.* 2021).

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3CaSO_4.2H_2O$$

Calcium sulfate can also appear as a secondary material in the production of boric acid from the raw material colemanite (Titiz-Sargut *et al.* 2007).

$$Ca_2B_6O_{11}.5H_2O + 2H_2SO_4 + 6H_2O \rightarrow 6H_3BO_3 + 2CaSO_4.2H_2O$$

The resulting mixture is then subjected to solid-liquid separation, typically through a filtration process, to separate the solid calcium sulfate from the liquid phase. Calcium sulfate product can be further processed and purified as needed for its intended application. The production of calcium sulfate as a byproduct of industrial processes is an economical way to utilize waste materials and reduce environmental impact. However, the purity and quality of the resulting calcium sulfate product may vary depending on the source material and the specific industrial process used.

Likewise, in the case of zinc mining, where calcium hydroxide is added to solutions containing zinc sulfate, the sulfate combines with calcium to form calcium sulfate (Rowe & Binnie 1974).

$ZnSO_4 + Ca(OH)_2 \rightarrow Zn(OH)_2 + CaSO_4$

1.2.4 Synthetic production

Calcium sulfate can also be produced synthetically by reacting calcium oxide (quicklime) with sulfur dioxide. This process produces calcium sulfate in the form of anhydrite, which can be further processed to produce other forms of calcium sulfate, such as hemihydrate or dihydrate. The following is a general overview of the synthetic production process:

Preparation of reactants: Quicklime (CaO) and sulfur dioxide (SO_2) are prepared and measured in the desired quantities.

Reaction: Quicklime is added to a reactor vessel and sulfur dioxide is introduced into the reactor at a controlled rate. The reaction between calcium oxide and sulfur dioxide produces calcium sulfite ($CaSO_3$).

$CaO + SO_2 \rightarrow CaSO_3$

Oxidation: Calcium sulfite is then oxidized to produce calcium sulfate. This is typically accomplished by bubbling air or oxygen gas through the reaction mixture, which converts the calcium sulfite to calcium sulfate.

$CaSO_3 + 1/2O_2 + H_2O \rightarrow CaSO_4 \cdot 2H_2O$

The synthetic production method allows for the production of high-purity calcium sulfate with consistent quality and physical properties. The process is also relatively

flexible, allowing for the production of different forms of calcium sulfate (such as hemihydrate or anhydrite) by adjusting the reaction conditions. However, the process requires specialized equipment and may be more costly compared to other production methods (Gao *et al.* 2020).

Overall, the production method for calcium sulfate depends on the desired properties of the product and the available raw materials and equipment. Each production method has its advantages and disadvantages in terms of cost, purity, and environmental impact.

1.3 Solubility

Calcium sulfate's solubility depends on the temperature of the solution. At room temperature, calcium sulfate is sparingly soluble in water, with a solubility of about 2.1 g/L. However, as the temperature of the solution increases, the solubility of calcium sulfate decreases.

In addition to temperature, the solubility of calcium sulfate is also affected by the pH of the solution. In acidic solutions, calcium sulfate is more soluble due to the formation of calcium bisulfate, while in alkaline solutions, it is less soluble (Shukla *et al.* 2019).

The solubility of calcium sulfate is also affected by the presence of other ions in the solution. For example, the presence of sulfate or chloride ions can decrease the solubility of calcium sulfate due to the formation of insoluble salts (Titiz-Sargut *et al.* 2007).

The pH has an effect on the growth of calcium sulfate crystals, thus reducing the solubility in the solution. Also, at higher temperatures, the solubility of calcium sulfate decreases, which leads to its precipitation and calcification, this in turn leads to some industrial problems (Titiz-Sargut *et al.* 2007).

The degree of solubility of calcium sulfate in solutions is very important and effectively affects the nucleation, formation and growth of crystals. There are some factors that can affect the degree of solubility in solutions, including organic and inorganic additives, temperature of the solution , ionic concentration and the pH of the solution (Shukla *et al.* 2019).The organic and inorganic additions of the calcium sulfate reaction medium directly or indirectly affect on the solubility of compounds in the solutions also the calcium sulfate compound. Where some of these additives increase the solubility of calcium sulfate compound in solutions, and others work to reduce the solubility of calcium sulfate compound and inhibit the crystallization process. When alcohol is added to the aqueous solution with or without NaCl, the solubility of calcium sulfate will decrease.

1.4 Calcium Sulfate Usage Areas

These are just a few examples of the many usage areas of calcium sulfate. Its versatility and wide availability make it a valuable material in many different industries. Calcium sulfate is used as a construction material for making gypsum board, plaster, and other building products. It is added to cement to regulate its setting time and improve its workability. It is used as a soil amendment to improve soil structure and fertility. It can also be used as a source of calcium and sulfur for plants. Also, it is used as a food additive to enhance the texture, flavor, and shelf life of foods. It is commonly used as a firming agent in cheese, tofu, and other dairy products. In addition, it is used as an inactive ingredient in pharmaceutical tablets and capsules. It can also be used as a desiccant to absorb moisture and maintain product stability. Of course, it is used in dental impression materials and as a bone grafting material in oral surgery as same a mold-making material in art and sculpture. It is used as a coagulant in water treatment to remove impurities and clarify water, too.

The calcium sulfate compounds are very important. The gypsum is one of this compound. Its mass is not compressed and contains many internal pores. Its crystals take needle and plats shapes, which increases its inner surface area. This gives it great importance in industry and in various applications. Calcium sulfate was used in dental

treatment because of its composition that is highly compatible with the structure of the teeth, as it was used as a filling for the teeth, It is completely absorbed after implantation (Anson 1998). One of the important considerations that cannot be overlooked when implanting a substance or compound inside the body is the biocompatibility with the body, and calcium sulfate has this property more than other materials and compounds (Bell 1964, Kelly *et al.* 2001, Lillo & Peltier 1956, Scarano *et al.* 2007). It may cause minimal infections after implantation in teeth or bones (Lillo & Peltier 1956, Schaffer 1971). Calcium sulfate dihydrate is used to deliver medicine to the body, where some types of drugs can be mixed with CSD to treat a number of bacterial infections, including infections of the bones and joints in humans (Doadrio *et al.* 2004). There are many drugs that can be combined with CSD.and since the structure of gypsum is similar to the skeletal structure of bone, biocompatibility, ease of use of gypsum and low cost, CSD was used in bone repair and grafting (Horowitz *et al.* 2014), where CSD is absorbed by the bones and without major infections (Orellana & Puleo 2014). Another area in which calcium sulfate has been used with remarkable success is to replace bone wax, (the substance on the surface of the bones that controls bleeding there) (Baird *et al.* 2018, Das 2018). Since the body's sensitivity to gypsum is little or no,the gypsum has been used in splinting and straightening fractures (Szostakowski *et al.* 2017). Gypsum has been used to fix the limbs in molds to reduce the pain resulting from fracture and keep the fracture from deformities that may occur as a result of movement (Sharma & Prabu 2013).

Where gypsum boards are used as an insulating material to protect buildings, laboratories, and others, because gypsum boards When exposed to heat, it begins to lose the water of crystallization inside it.This acts as a great inhibition or prevention process from the occurrence of fire, and thus the damage resulting from fires is reduced (G. Thomas 2002). Agricultural soil specifications are also improved by adding calcium sulfate, which is used as a fertilizer, as it is a source of calcium (Ca^{+2}) and helps absorb sulfur dioxide (SO_4^{-2}), which increases its absorption by the soil as a result of increased calcium absorption. Calcium sulfate is also considered safe for human life, so it is used in many food industries such as tofu. It is considered a coagulant and fermented substance and is used in the manufacture of cheese (Jayasena *et al.* 2014). Gypsum is

used to improve some types of cement and the Portland cement industry, which is a common type of use (Heimann 2010) as it is widely used in construction in roads, building structures, bridges and other structures (Olson 2001), where when gypsum is added to (OPC) ordinary Portland cement. It works to inhibit the interaction with water (Bhanumathidas & Kalidas 2004), which ensures that the (OPC) remains in the plastic case for a longer period so that construction professionals can handle it more easily.

Also, when water is added to gypsum at a normal temperature representing room temperature, it turns into dihydrate, which has a relatively large hardness, which makes it easy to form and manufacture different forms of it and its uses were varied, such as sticks (blackboard chalk) for medical uses such as fixing broken bones and dental purposes and making molds that are used in metal casting and shaping.

It is also used for civil construction purposes, such as building dams in mines. It is also used in the manufacture of marble, alabaster, floor plaster, marble cement and Barian cement (casting gypsum with borax) (López-Buendía et al. 2020). There are many applications and industries in which calcium sulfate plays a major role and is a basis in these applications, but we cannot mention them all.

1.5 Disadvantages

Due to the difficulty of removing calcium sulphate deposits by mechanical methods and common solvents, one of its common harms is that it collects on the surfaces of equipment, which leads to equipment damages, impedes production processes and reduces their efficiency (Shukla *et al.* 2019). Such as calcium sulfate is deposited on the outer surfaces of evaporation equipment, which leads to a reduction in the efficiency of evaporators, which leads to the need to clean them frequently (Linnikov 1999). Crystallization of calcium sulfate on the surfaces of the reverse osmosis (RO) membranes, which leads to a decrease in the efficiency of the flow and may lead to the damage of the reverse osmosis membranes (Lin *et al.* 2011).

One of the damages caused by calcium sulfate is its deposition on the outer and inner surfaces of the pipes in the heat exchangers, which leads to the prevention of heat exchange and the lack of proper energy transfer, and at the same time increases the risk of high temperatures inside the heat exchanger, it's deposition inside the pipes leads to a reduction the internal diameter of the pipes, thus reducing the flow in these pipes, increases the pressure on the operating pumps, where the corrosion caused by some deposits leads to damage to the metal parts of the equipment (Doğan *et al.* 2004). As many studies have shown, there is a transient toxic effect of calcium sulfate, which causes some inflammatory reactions (Coetzee 1980, Lee *et al.* 2002, Robinson *et al.* 1999, Strauß 1999).

1.6 Objectives

This study attempts to achieve the following objectives:

1. Knowing the effect of changing the concentration of the reactants on the nucleation period and growth rate of calcium sulfate crystals.
2. Knowing the effect of changing the concentration of (poly (sodium 4-styrene sulfonate) PSSS added to the reaction on the nucleation period and growth rate of calcium sulfate crystals.
3. Knowing the change in the concentration of the reactants on the morphology of calcium sulfate crystals
4. Knowing the effect of changing the concentration of poly (sodium 4-styrene sulfonate) (PSSS) added to the reaction on the morphology of calcium sulfate crystals.

1.7 Scope

Due to the importance of calcium sulfate and its wide uses, there have been numerous studies on the nature of its crystallization, the beginning of crystal formation, crystal growth. The study of methods that accelerate the crystallization process and the production of crystals of different sizes was studied, also been studied what factors have

an effect on the production and morphology of crystal formation and the effect of different reaction medium and organic or inorganic additives, to obtain the highest precipitation rates and the desired sizes of crystals according to their use in different fields. On the other hand, due to the damages caused by the sedimentation and calcification of calcium sulfate in some industrial sites, there were studies to discourage the crystallization process, the control size of the crystal and the shape of the crystals?

Quite a few researchers have researched and studied the factors that affect the morphology and growth of crystals in low-soluble salts, that was these factors were organic or inorganic additives in addition to other physical factors such as temperature, saturation rate, seeds and hydrothermal reactions (Abdel-Aal 1989, Deng *et al.* 2009).

This research comes in the process of studying and increasing knowledge about the extent of the influence of the Psss on crystal formation, growth, and morphology as well as the effect of changing the reactants on the reaction rate, crystal growth and crystal formation as a complementary step to what other researchers have done.

2. LITERATURE REVIEW

Calcium sulfate is one of the compounds that have wide uses in various industrial fields such as insulators, molds industry, building materials, etc. Or the extraction of some minerals and as a byproduct of chemical reactions such as the process of getting rid of sulfur in fossil fuels, in the case of zinc mining, where calcium hydroxide is added to solutions containing zinc sulfate, sulfate combines with calcium to form calcium sulfate, and sometimes calcium sulfate is found in nature, containing some ımpurities that must be disposed of before use, such as silicate, strontium, lead, And some other natural elements (Ricci *et al.* 2000). For the importance of calcium sulfate, it should attract wider research interest, and in the future there should be a wide field of research in this compound to reach better properties and better methods of preparing or inhapeted the formation of this compound as needed.

Many researchers have conducted experiments and written research for the crystallization of calcium sulfate and how to control crystal formation, growth speed, crystal formation morphology, and studying the factors affecting these properties of concentrations of solutions, organic and inorganic additives, the type of medium in which the reaction takes place, the effect of seeds, super saturation and temperature for what It is of great importance and wide areas of application, some of which are commercial applications and others industrial and treatment great and they had important results in this field .It is known that the impurities that are present in the solution during the crystallization process have an effect on the formation of crystals as well as have an effect on the growth rate of crystals, it may have a negative effect or a positive effect on the growth rate and often leads to a delay in the growth rate of crystals. In spite of this knowledge, there were studies to find out this effect on the course of the reaction and on the shape of the crystal. Among the additives that were studied were additives with a low molecular weight such as dyes (Smith & Alexander 1970) and some surface activating agents (Michaels & Colville Jr 1960) or the additives are in the form of charged ions (Gilman 1963, Kressman & Kitchener 1949). There was interest in the polymers as impurities for use as inhibitors in the formation of calcium sulfate dihydrate crystals (Ridge & Surkevicius 1962).

But despite this, there is a lot of ambiguity about how this salt was formed due to the change in the conditions surrounding the reaction from the temperature of the solution, the pH value, the ionic strength, and the presence of impurities such as foreign ions in water. Soluble compounds. We include below some of this previous literature:

Wang and Chen et al in the 2018 studied the changes that occurred in the crystallization of calcium sulfate whiskers in the presence of different percentages of impurities and knowing the morphology of the formation and the ratio of length to width. It was found that when the percentage of impurities increases, the ratio of width to height begins to decrease. It was also noted that calcium sulfate is formed in different forms, there is the type that takes the shape of a needle and the other type takes the form of rods, and it has been confirmed that the impurities have an effect on the crystallization process, significantly through the change in the crystal structure (S. Wang *et al.* 2018).

Ö. Doğan, E. Akyol, and M. Öner in 2004 found that the polymers, even if they are in very small quantities, 1 ppm, they lead to an initial inhibition at the beginning of the reaction called the induction period. The duration of the induction time was identified through the continuation of the decrease in the conductivity of the solution. It was also noted that the increase in the concentration of polymers in the solutions leads to an increase in the induction time. There is also an effect of polymer additions on the shapes of gypsum crystals, when not added, gypsum crystals take needle shapes and when polymer is added, they take the shapes of plates or similar to plates (Doğan *et al.* 2004).

McCartney and Alexander in 1958, studied the addition of polymers to the reaction of calcium sulfate crystal formation. It was observed that the polymers that include the carboxyl group in their composition have a particular effect on inhibiting the reaction to form calcium sulfate crystals, such as alginic acid, carboxymethylcellulose, polyaerylie acid and polymethaerylic acid. They were also found when using the same concentration of polyaerylic acid is more active than using polymethaerylic in inhibiting

the reaction. It was also observed that there is an effect of the pH of the reaction solution on the inhibition strength (McCartney & Alexander 1958).

Smith and Alexander in 1970, the results of their study indicate that the induction period is longer in the case of adding a different concentration of polyacrylic acid (PAA), and the induction period increases with the increase in the concentration of the additive, and the growth rate decreases and the reaction becomes slower in the presence of the additive, as it works to inhibit the reaction and the formation of the crystals The size of the precipitation is smaller compared to the size of the crystals without the addition, as the size of the crystals is inversely proportional to the size of the concentration of the additive (Smith & Alexander 1970).

Maria G. Lioliou, Christakis A. Paraskeva et al. in 2006 studied the effect of adding polyacrylic acid (PAA, three different polymers) and a copolymer of polystyrene sulfonic acid PSA to supersaturated calcium sulphate solutions at a temperature of 25 °C. They noted that in the presence or absence of the polymers, calcium sulfate will precipitate, but with the presence of polymers, the induction time will increase directly with the increase in the concentration of the polymers, and the rate of sedimentation decreases also that there is a relationship between the molecular weight of the added polymers & the inhibition efficiency, as it was noted that the lower the molecular weight of PAA, the greater the inhibition efficiency and the lower the precipitation rate. Also, The presence of polymers has The reaction solutions influence the morphology of the crystals (Lioliou *et al.* 2006).

Chen Wang, Tingting Shen, Shuping Li and Xikui Wang in 2014, they studied the effect of a low-phosphorus polymer as an inhibitor of the reaction and formation of calcium sulfate hydrate crystals. They found that when increasing the concentration of the polymer, the rate of inhibition of the reaction will increase significantly and the precipitation of calcium sulfate dihydrate crystals will decrease. They also found that there is a relationship between the degree of polymer viscosity and the molecular weight of the polymer with the rate of inhibition. When the rate of viscosity and molecular weight decrease, the rate of inhibition will increase. when the calcium sulfate precipitate

has examed by scanning electron microscopy (SEM), they noticed that the growth rate of the formed calcium sulfate crystals decreased, and the (XRD) examination showed that there is a change in the shape of the crystal formed in the presence of the new low-phosphorus copolymer (C. Wang *et al.* 2014).

Neira-Carrillo et al. in 1988 studied the crystallization of $CaSO_3$ in the presence of conductive polymers and knowing its effect on crystallization, as it appeared that the structural placement of the polymer has a clear effect on crystallization (Neira-Carrillo *et al.* 2008).

Sevgi Polat and Perviz Sayan made a study in 2017 to find out the effect of carboxylic acids on the crystallization of calcium hydrosulfate. They found that the filtration rate is affected by the addition of carboxylic acids. The filtration rate varies from in pure media, meaning the presence of carboxylic acids in the aqueous solution on the calcium hydrosulfate crystals in the impure aqueous medium, where the crystals absorb the acids carboxylate on the surface of the crystal. It was found that the addition of carboxylic acids affects the morphology of calcium hydrocarbon crystals, as it changes the shapes they take in pure solutions (Polat & Sayan 2017b).

S. Polat and P. Sayan in the year 2017 studied the effect of adding trimesic acid on the crystallization of calcium hydrosulfate and found that when adding small amounts estimated at parts per million of trimesic acid, this addiction affects the rate of crystal growth and leads to a decrease in the filtration rate and notes it changes the ratio length/width in the formation of crystals (Polat & Sayan 2017a).

Anduix-Canto et al. in 2021, studied the deposition of gypsum in aqueous media with nanoscale sizes so that it could not change its positions and grow slowly in its positions. It is possible to follow the nucleation and growth by tomography without the need to isolate the crystals, as well as the use of the method of diffraction by means of synchrotron rays. Where it was shown that the induction time of Bassanite ($CaSO_4 \cdot 0.5H_2O$) is long by observing it in nano-media, as well as gypsum $CaSO_4.2H_2O$

can be precipitated by various paths without damage to the crystal structure (Anduix-Canto *et al.* 2021).

OD Linnikov in the year 1999 make astudy, in this study was conducted for the purpose of knowing how calcium sulfate crystals are formed on the metal surfaces of machines and equipment, especially those with hot surfaces due to the nature of their work such as the heat exchanger and within the electronic solutions.Study of the effect of surface roughness on the nucleation and growth period of calcium sulfate. The method of light changes and the amount of current reflected from the surface was used to determine the growth in the calcium sulfate nucleus. It was found that the surface roughness has an effect on growth, as increasing the surface roughness increases the growth of the calcium sulfate nucleus. It was also noted that there is a nucleus that forms on the surface of the mineral and is the center of the formation of several other crystals.When the crystallization temperature increases, the rate of supersaturation increases, which leads to an increase in crystals splitting and forming (Linnikov 1999).

Nancy and Wen-Yi et al. in 2011 made a study to identify the effect of the topography of the surface on which calcium sulfate crystallizes, as well as the effect of the chemical composition of the surface on the crystallization process and the growth of calcium sulfate crystals. Experiments were carried out on a number of polymeric surfaces. Experiments were carried out on the micro-quartz system (QCH), and the level of gypsum gathering on the rougher surfaces was higher than on the less rough surfaces, and the nucleation rate and growth rate increased in the rougher surfaces. It was also noted that in surfaces that have the same degree of roughness, but differ in terms of surface chemistry, there is a difference in the size, density and number of the crystals formed. This means that surface chemistry has an effect on surface crystallization. This study shows the possibility of controlling crystallization through the selection of surface topography and surface chemistry (Lin *et al.* 2011).

Shukla et al. in the 2019, studied the effect of alcohol on the solubility of calcium sulfate dihydrate (gypsum - $CaSO_4.2H_2O$). It was found that when adding alcohol, the dissolution of calcium sulfate in an aqueous sodium chloride solution was significantly

reduced, and the solubility was maximumimum in a lower concentration of sodium chloride. and using the least-squares method, the experimentally determined physical and derivative properties were linked. It was also concluded that alcoholic hosts are environmentally friendly and low cost they reduce the solubility of gypsum in aqueous systems with or without sodium chloride. In the solution without any additive when the increase in the concentration of calcium chloride to reach a maximumimum leads to increases in the solubility of $CaSO_4.2H_2O$ and then starts decreasing when adding Alcohol into the reaction medium a decrease in the solubility of the salt is observed as a result of the reaction with the electrolyte with increasing concentration. They also noted the possibility of water molecules forming a strong hydrogen bond with alcohol. Because of this bonding, these strong hydrogen bonds reduce the free water molecules leading to a decrease in the solubility of $CaSO_4.2H_2O$, as well as a decrease in the empty spaces, and thus the density of the number of Ca^{+2}, SO_4^{-2} ions decreases. By examining gypsum crystals produced from aqueous alcohol solutions by FE-SEM, the surface formation of these crystals was known. When make SEM examined the crystals and the availability of images, it was observed that there was no effect of the alcoholic additives on the crystal formation process or the formation of those crystals, and there was no effect on the solid crystals. It was also observed that due to surface adsorption, some crystals were thicker than others since gypsum has solubility lower than that of NaCl. This leads to the crystallization of gypsum before NaCl. Gypsum crystals crystallize in aqueous sodium chloride solutions, so sodium ions are partly involved in forming the structure of gypsum (Shukla *et al.* 2019).

Baohong and Guangming et al. in 2011 studied the effect of ethanol alcohol concentration value on the formation of α-calcium sulfate hemihydrate. Under atmospheric pressure in the methanol–water solution, they noticed that the temperature of formation of hemihydrate in pure water and under atmospheric pressure is high. As for using methanol–water solution, the temperature is lower because methanol is able to lower the temperature of formation. I also note that the growth rate increases and then the nucleation speed increases with the increase in methanol concentration. Since the growth rate depends on super saturation and temperature, this makes super saturation pushes to crystal growth and thus to an increase in nucleation. Increasing the

concentration of methanol can affect the super saturation and thus represent an impetus for growth and nucleation. They also found in certain concentrations of methanol the concentration of methanol affects the water content in the crystal structure, and the effect of inhibition can occur as a result of adsorption and adhesion on specific sites of the crystal face (Guan *et al.* 2011).

Sandhya et al. in 2012 studied the low-dimensional calcium sulfate dihydrate crystals obtained from sulfuric acid-calcium nitrate system using isopropyl alcohol as an organic solvent. The crystals formed were rods. It was found that the material included is pure calcium sulfate dihydrate and it was detected using X-ray diffraction and infrared spectrometry of the transform the material is well crystallized. Through the classical nucleus theory to deduce the parameters, the nucleation movement and the induction time of the solutions were monitored. The data were analyzed to know the interfacial tension, nucleation rate and critical radius. As for the surface energy of aqueous precipitation, it is less than the reported energy. It is possible that this change in the energy value is due to the presence of isopropyl alcohol. It was also noted that the nucleation rate increased significantly, while the critical radius decreased significantly with the increase in the percentage of supersaturation. It was also observed when performing the photodispersion decomposition that the particles had a monomodal distribution.In clinical medical applications, calcium sulfate dihydrate, which is uniformly crystalline and has low dimensions, can be used for bone grafting and drug delivery (Sandhya *et al.* 2012).

Tushar, Pratiksha, and Arvind Kumar in 2013 were study the effect of organic solvents on sulfuric calcium dihydrate ($CaSO_4.2H_2O$) in sodium chloride solution was studied. There was a change in solubility when adding some organic solvents, such as when adding EA ethyl acetate, which led to an increase in the solubility of calcium sulfate dihydrate and some organic solvents such as glycerin Gly made a small change, and some of the organic solvents such as (DMF, IPA) reduced the solubility of calcium sulfate dihydrate, as the maximumimum solubility needed higher concentrations of NaCl in the case of using the organic solvent IPA. It was noticed that the crystals of calcium sulfate dihydrate were made in different shapes. They were rod-shaped with the

organic solvent EA, they were in the form of thin, flower-like needles, and they were in the form of small needles with the organic solvent IPA, and they were crystals with a rough surface with the organic solvent DMF. The shapes of the crystals differed in the use of organic solutions with NaCl, crystals were formed in shapes (thick hexagonal rods), which means that organic solvents have an effect on the precipitation, growth and formation of calcium sulfate (Trivedi *et al.* 2013).

Zongyou, Yi Loua and Guangyong et al. in 2013 studies the effect of adding ethanol to the reaction medium was known by observing the beginning of the sedimentation time. It was noted that the addition of ethanol reduces the solubility of the calcium ion (Ca^{+2}) and thus reduces the sedimentation time of CSD. When R reached 1 the addition of more ethanol does not have a noticeable effect on the beginning sedimentation time. The addition of ethanol increases the speed of the reaction between H_2SO_4 and $Ca(OH)_2$ and increases the production of CSD, and different shapes of crystals (sheets, rods, or thick crystals) appeared as a result of adding ethanol, which indicates that adding ethanol has a strong effect on crystal formation and modifying the dimensions of the crystals and the size distribution of the crystals (Pan *et al.* 2013).

Yehia, Ali and Kandil in 2011, studied the effect of super saturation (1.2 - 2) on the crystallization of calcium sulfate at pH 3, ionic strength of 0.5 M and at 80 °C. It was noted that aluminum and manganese nitrate in low concentrations delay the crystallization rate in proportion to their quantity. It was also noted that the crystallization rate depends on the stirring rate and that temperature has a direct effect on the crystallization rate. The higher the temperature, the higher the crystallization rate, as well as the increase in pH 3-10 affect the increase in the rate of crystallization in the compound calcium sulfate (Yehia *et al.* 2011).

Xiao and Liushuan Yangb et al. turned their attention to their study of Effect of calcium sulfate whiskers resulting from the removal of sulfur from the flue gas by changing the reaction medium. When calcium chloride and sulfuric acid are used in the reaction to increase growth and adjust the reaction medium. It was noted that calcium sulfate whiskers grow in the medium ($NaCl-H_2O-H_2SO_4$) using FGD gypsum as a raw material.

It was also observed that this medium, which contains calcium chloride and sulfuric acid, affects the solubility of gypsum FGD. Also, in this solution, the concentration of calcium ion Ca^{+2} and sulfate ion SO_4^{-2} can be maintained stable. This means that by changing the concentration of sulfuric acid and calcium chloride, the crystallization of products can be controlled by hydrothermal (X. Wang *et al.* 2014).

S. Titiz-Sargut in 2007, in his study Calcium sulfate hydrate was monitored in reaction medium under varying conditions of pH, temperature and different concentrations of citric acid, where pure $Ca(OH)_2$ was reacted with H_2SO_4 solution, where the filtration rate and crystal size distribution were calculated as a function of citric acid. From the results of CSD and SEM, it was indicated that pH has an effect on the size and distribution of particles, as well as that pH has an effect on the morphology of gypsum, as the pH affects the shape of the crystal, the shell of the crystal changes according to pH, which gives great importance to pH is that the filtration depends on the size and thickness of the crystal. They found that the shape of the crystals is needle-shaped at pH 2.5, while the shape of the crystals is larger and thicker, pH 3, so the pH 3.5 was chosen as ideal for the experiments (Titiz-Sargut *et al.* 2007).

Smith and Sweett, in their study have got some results. Through the results obtained, it was noted that the stirring conditions have an effect on the rate of crystallization, but its effect is slight, as the failure to stir at the required speed and in a good way will affect the homogeneity of the nucleation and the induction period. It was also noted that not doing the required stirring rate affects the volume The surface area available for the growth rate, which allows for a high growth rate, where to the calcium ions dry on the crystal surface lead to reduces the effective growth rate (Smith & Sweett 1971).

Singh and Middendorf in 2007, they studied the hydration of the calcium sulfate semihydrate ($CaSO_4.1/2H_2O$) was studied, which leads to the crystallization of gypsum $CaSO_4$ dihydrate. The water properties, hydration mechanism and crystal growth of gypsum were discussed, as it was found that the additives change the liquid molecular structure of the hardened gypsum and makes it less strong than it was. Among the results obtained, the reactions that take place when hydrating the hemidates are

exothermic and there is a difference in their paths due to several factors, including the method in which the surface is prepared for the reaction, the surface area of the reaction surface, crystal size, the presence of defects, and topography on the surface. The water reactions were also controlled and controlled by controlling the nucleation, which leads to the growth of crystals and obtaining structures that give strength to the crystal structure it has interlocking structure. How much was observed when adding substances to the reaction that change the nucleation rate, either increasing the nucleation rate or reducing the nucleation rate and thus changing the microstructures, which leads to a change in the chemical and physical properties (Singh & Middendorf 2007).

Ulrich, Alexander and Andreas Kempter et al in the 2015 precipitated calcium sulfate in an alcoholic medium containing low concentrations of water. They were able to change the distinct polymorphism and adjust the result of the reaction by freely adjusting the amount of water in the mixtures. $CaSO_4$ is produced from any phase in the pure state or the water of crystallization dimer in Mixtures with predetermined formulations. This means that the phase selection in $CaSO_4$ mineralization is possible.

Smith and Sweett in 1971, studied the crystallization expansion of calcium hydrate in the absence of seed crystals added to the nucleus. Calcium sulfate crystals were heterogeneous, and the growth rate was proportional to the surface of the crystal region and the super saturation square. The experiments also showed that the crystallization rate is affected slightly under the conditions of stirring. With an increase in the stirring rate, the growth rate approaches the stability of the value, and that in the high rate of volatility the diffusion cannot be controlled, and the kinetic importance of surface processes has appeared in the beginning of crystallization (Smith & Sweett 1971).

H. El-Shall and M. M. Rashad in 2002, added Aminotris methylene phosphonic acid (ATMP) to the reaction medium when producing phosphoric acid from phosphate rocks to know the effect of this addition on the induction time, growth rate, and formation of calcium dihydrate crystals in order to be able to achieve a higher filtration rate, which leads to a higher production rate of phosphoric acid. They used supersaturation rates in different degrees, calculated the surface energy at different supersaturation rates, and

calculated the critical basic size and crystal growth rates of gypsum. Through this, it was observed that the induction time decreases when supersaturation is increased and that the addition of (ATMP) leads to a decrease in the surface energy compared to lack no addition of (ATMP). Which means that some additives have an effect on the shape and size of the crystals, which calls us to study new additions to know their effect on the crystallization of calcium dihydrate sulfate (El-Shall *et al.* 2002).

Marina, Amedeo, and Dino Musmarra conducted a 2003 study to find out the ability of citric acid when added to the reaction medium to inhibit the nucleation of calcium sulfate in the use of supersaturated solutions and by using different percentages of citric acid. The nucleation time and when the temperature increases with the same percentage of saturation, its effect is reverse, meaning that the induction period increases and the nucleation time increases. It was also noted that the effect of citric acid is stronger when the temperature is low on the time of induction, which means when the temperature decreases and the time of induction decreases, the effect of citric acid increases and is strong to inhibit the nucleation of gypsum. Citric acid is one of the additives that have an effect on the nucleation of gypsum (Prisciandaro *et al.* 2003).

Yubin Wang and Xinyu Mao et al. in 2020, in their study of the effect of sulfuric acid when preparing filaments of calcium sulfate semihydrate from calcium sulfate dihydrate, it was observed when using sulfuric acid concentration under constant conditions of temperature and reaction time. Crystals are formed in different shapes depending on the change in the concentration of sulfuric acid. It was noted that the acid had a specific effect and in a dramatically. It was also noted that sulfuric acid had an effect on the solubility of calcium sulfate dihydrate, as well as working to increase the supersaturation of calcium sulfate semihydrate (Y. Wang *et al.* 2020).

Zhilong Zhu and You Peng, et al. in 2016 in thier article The simulation method used in the interactive crystallization of gypsum differs from other methods as it is more efficient in computational terms. To know the effect of impurities (metal ions) on growth, nucleation and supersaturation, the induction time, nucleation rate and growth rate of crystals were monitored and measured in several experiments with different acid

concentrations and different temperatures. It was observed that when nucleation increases and the surface area of crystals increases becouse nucleation, supersaturation decreases. Also, when supersaturation reaches a state of equilibrium, the growth rate decreases, and the nucleation rate decreases. The results showed that the presence of impurities affects the shape of the crystal, which leads to a reduction in the average aspect ratio (Zhu *et al.* 2016).

Sebastain Jakub Gurgul got PhD degree in 2020 In his thesis, which dealt with the use of gypsum particles to increase the speed of transformation of calcium sulfate hydrate ($CaSO_4.1/2H_2O$) to the dihydrate ($CaSO_4.2H_2O$). This process has many applications. A number of studies have been conducted to better understand how the transformation process occurs and to develop new approaches to speed up the reaction rate. It was found that the most commonly used accelerator is finely ground raw gypsum. Since the properties of gypsum differ from quarry to quarry depending on the soil from which the gypsum is taken, and thus lead to the difference in the ability of the earth particles "seeds" to speed up the conversion process dramatically, so there was a need to find a way to produce seeds from the base to the top that allows using the same formula worldwide (Gurgul 2020).

3. MATERIALS AND METHODS

The reactants used in the experiments to synthesize calcium sulfate were chosen as calcium chloride dihydrate (ACS reagent >99%) and sodium sulfate (ACS reagent >99.5%). Solutions were prepared using reactants by mixing Type II water produced from Merck Millipore. All experiments carried out in aqueous media. Reactant concentrations are equamolar and concentrations of 0.02 M, 0.03 M, 0.04 M, 0.05 M, 0.06 M, 0.07 M, and 0.08 M were studied in experiment without additive. Then the reactant concentration was kept constant at 0.04 M in the present of additive. The additive concentration was varied between 0.001 g/L, 0.025 g/L, 0.05 g/L, 0.01 g/L, 0.05 g/L, 0.1 g/L, and 0.15 g/L (Table 3.1). The reactions were carried out in a 1 L jacketed glass-lid reactor and the temperature was kept constant at 30 °C during the experiments. A mechanical mixer (IKA Eurostar 20) was used in the experiments and the mixing speed was set as 300 rpm. The residue, which is filtered and dried after washing, was dried in a vacuum oven at 80 °C about 12 hours.

Table 3.1 Experiment plan

Exp. No	Reactant Concentration (mol/L)	Additive Concentration (g/L)
1	0.04	-
2	0.04	0.001
3	0.04	0.0025
4	0.04	0.005
5	0.04	0.010
6	0.04	0.050
7	0.04	0.100
8	0.04	0.150
9	0.02	-
10	0.03	-
11	0.05	-
12	0.06	-
13	0.07	-
14	0.08	-
15	0.04	0.250

XRD, SEM and BET analyses of the obtained powder were made. X-ray diffraction Bruker D8 Discover instrument was used in the investigation of the powder materials. Scans were conducted to select the 2Theta range with respect to approximate patterns found for $CaSO_4$ from the International Centre for Diffraction Database (ICDD). The 2Theta values were between 13° to 90°. SEM analyses were performed using Carl Zeiss Sigma 300 VP field emission scanning electron microscope. BET specific surface analyses were performed using the Quantachrome Nova Touch LX4 instrument.

4. RESULTS AND DISCUSSION

4.1 Investigation of Concentration Effect

XRD analyses show that the materials produced in all experiments consist of calcium sulfate in the form of Bassanite. Crystal morphology was monoclinic. Three type of Bassanite form was seen in XRD analyses: Calcium Sulfate (VI) 0.67-hydrate – Alpha, Calcium Sulfate Hydrate (1/1/0.6), and Calcium Sulfate Hemihydrate. Table 4.1 summarizes properties of these forms. Synthesized material with equimolar reactant concentration of 0.06 M has all the three type of Bassanite forms. Figure 4.1 shows XRD analysis of this condition.

Table 4.1 Properties of the synthesized Bassanite Crystals

Reference Code	Chemical Name	Chemical Formula	Calculated Density (g/cm³)	Volume of Cell (10^6 pm³)
98-001-1607	Calcium Sulfate(VI) 0.67-hydrate Alpha	$CaSO_4.(H_2O)_{0.67}$	2.80	1055.96
98-003-4677	Calcium Sulfate Hemihydrate	$CaSO_4.(H_2O)_{0.5}$	2.73	1058.07
98-002-8108	Calcium Sulfate Hydrate (1/1/0.6)	$CaSO_4.(H_2O)_{0.6}$	2.76	529.88

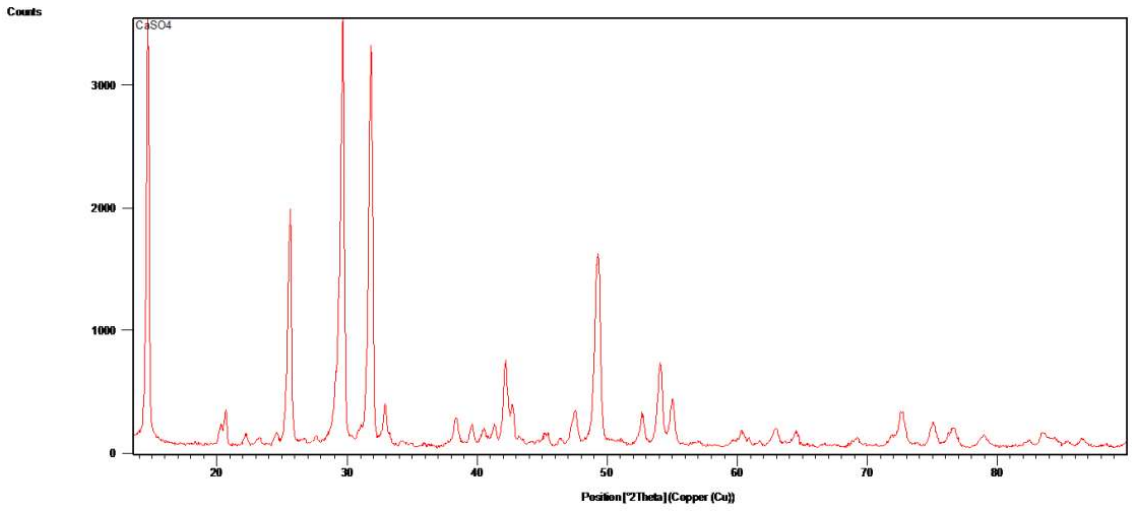

Figure 4.1 XRD analysis of synthesized material with equimolar reactant concentration of 0.06 M

Figure 4.2 shows the morphology of products under different concentration. Column-shaped and plate-like morphology are seen at 0.04 M concentration and the dimensions are quite high in both crystal types. Even if the morphology of the products is similar, the content of column-shaped products changes with increasing concentration. When the concentration is 0.06 M, there are more producs in the form of plate-like with less product from the short column-shaped and some needle-like crystal formed. When the concentration increased to 0.07, the content of needle-like products increased, but its length was short, and some plate-like crystals existed. When the concentration is further increased to 0.08, the content of plate-like decreased and the number of needle-like crystals increased. The concentration has a certain regulating effect on the crystal morphology of calcium sulfate hemihydrate, and the crystal size is smaller when the concentration is 0.08 M. In addition, when the initial concentration was tuned 0.08 M, the crystals, has needle-like morphology was appeared to be about 1 μm in width. Similar to this formation is also seen in the literature (Fukugaichi & Matsue 2018). As a result of the BET specific surface analysis, it was determined that the BET surface area of this material was 38.7 m^2/g.

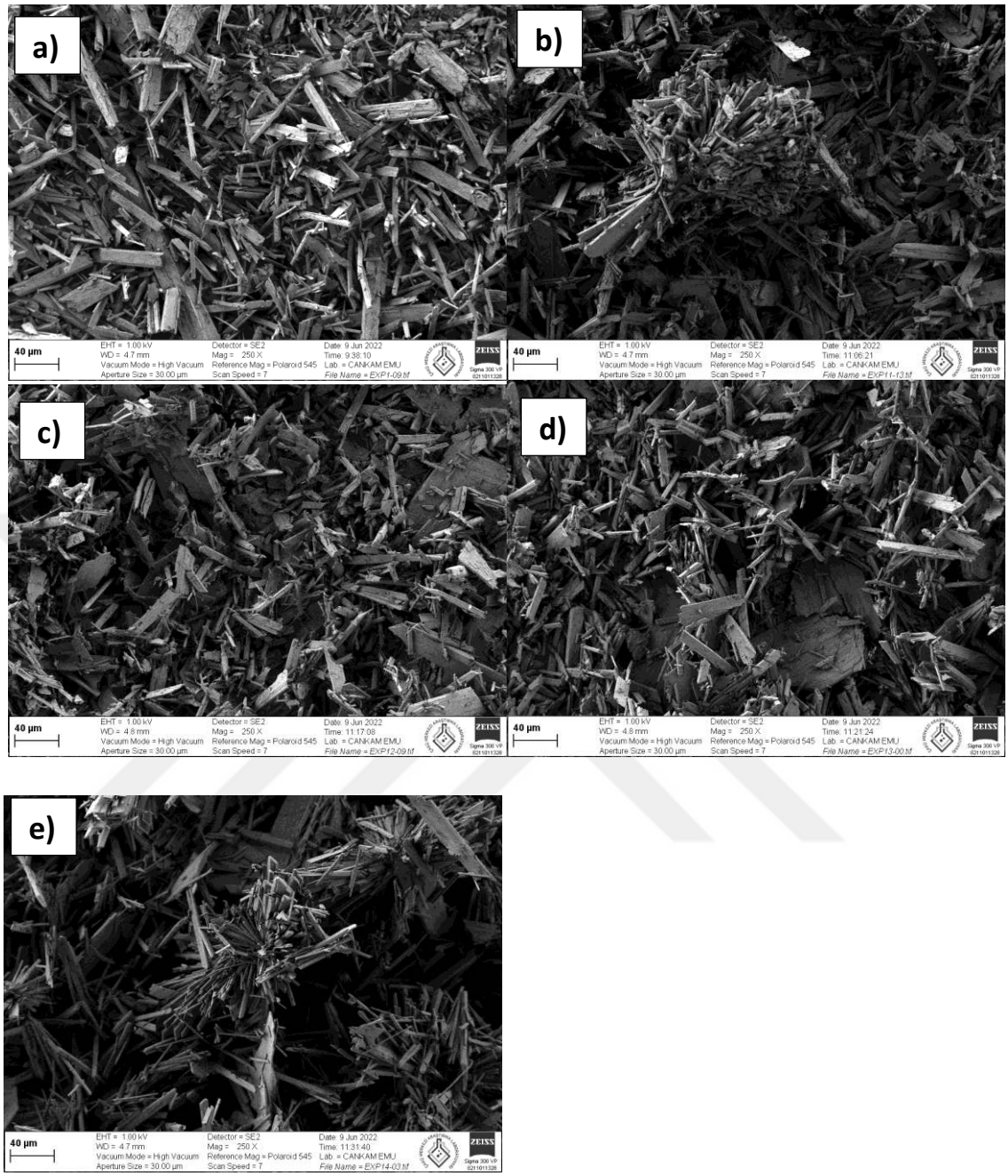

Figure 4.2 SEM micrographs showing the morphology of products under different concentration (a) 0.04 M; (b) 0.05 M; (c) 0.06 M; (d) 0.07 M; (e) 0.08 M.

When reviewing the results of the dimensional analysis using SEM separately for the produced crystals, the average values of width and height were found after conducting approximately one hundred measurements for each sample, and the size distributions

were revealed after conducting the analysis using SEM analysis of Exp1 are given in Figure 4.3.

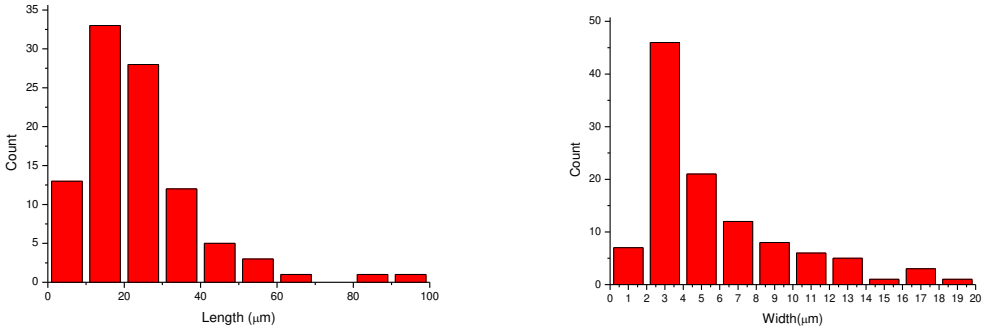

Figure 4.3 Size distributions of Exp1

The average length of the Exp1 material was 23.86 ± 15.85 µm. The minimum crystal length was 2.79 µm and the maximumimum crystal size was 96.98 µm. Similarly, the average width was 5.70 ±3.96 µm. Results based on measurements of SEM analysis of Exp1 material are summarized in Table 4.2.

Table 4.2 Descriptive statistics on Exp1

	N total	**Mean**	**Standard Deviation**	**Sum**	**Minimum**	**Median**	**Maximum**
Length	97	23.86121	15.85198	2314.53707	2.79299	21.17502	96.97939
Width	110	5.56979	3.95747	612.67734	1.0468	4.16256	19.21182

In Figure 4.4, the size distributions of the size measurements made from the SEM image of Exp11 are shown.

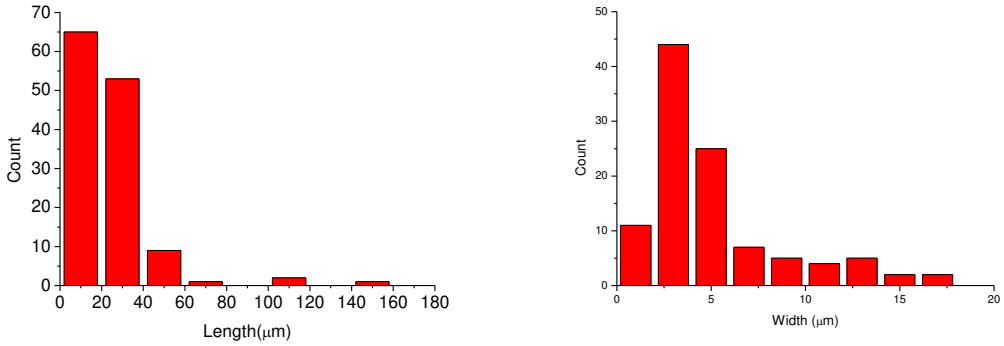

Figure 4.4 Size distributions of Exp11

According to these results, the mean height value was calculated as 25.21 ±19.63 μm and the mean width value was calculated as 5.11 ±3.64 μm (Table 4.3).

Table 4.3 Descriptive statistics on Exp11

	N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
Length	131	25.21316	19.62876	3302.92441	6.60471	20	158.98389
Width	105	5.11501	3.64443	537.07559	1.37546	3.89095	17.2119

Figure 4.5 shows the size distributions of Exp12 obtained by size analysis using the same method.

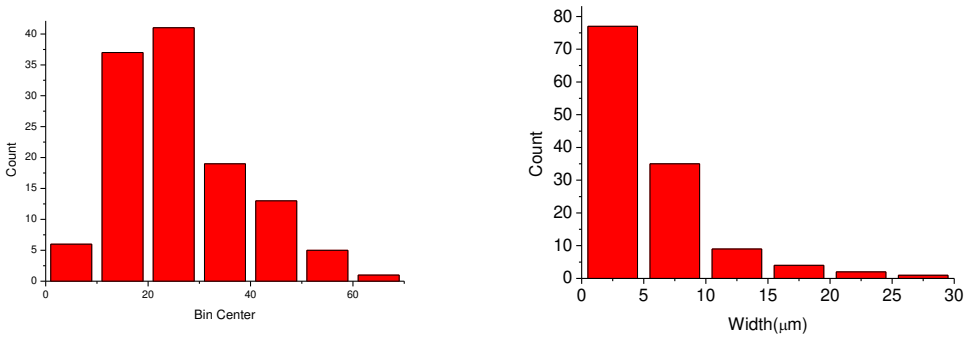

Figure 4.5 Size distributions of Exp12

A summary of the statistical data of the Exp12 material is given in Table 4.4. The data show that the average length of the material is 26.51 ±12.17 µm and the average width is 5.57 ±4.70 µm.

Table 4.4 Descriptive statistics on Exp12

	N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
Length	122	26.51292	12.17307	3234.57635	1.02217	24.32882	61.2069
Width	128	5.57006	4.69884	712.96798	0.86207	4.02709	28.76847

The size distributions of the material coded as Exp13 are shown in Figure 4.6.

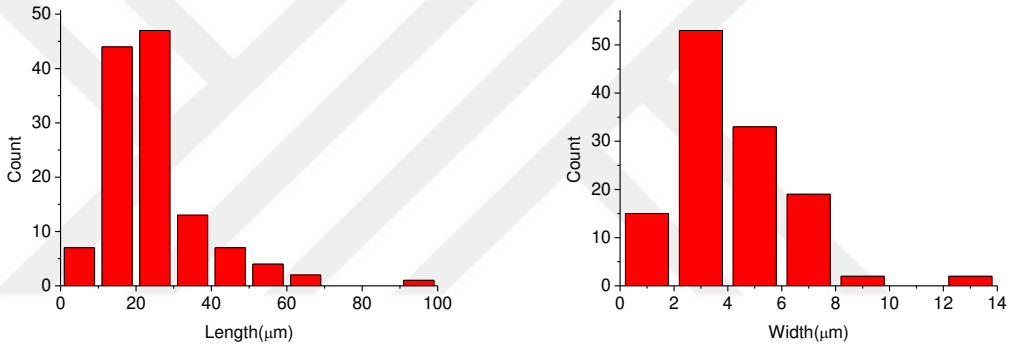

Figure 4.6 Size distributions of Exp13

According to the statistical data of the material coded as Exp13 given in Table 4.5, the average length is 26.55 ±13.00 µm and the average width is 4.17 ±2.17 µm.

Table 4.5 Descriptive statistics on Exp13

	N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
Length	125	26.55444	12.99842	3319.30534	9.38561	22.90831	90.8058
Width	124	4.17333	2.16792	517.49305	1.06206	3.80364	13.48564

The size distributions of the material named Exp14 are shown in Figure 4.7.

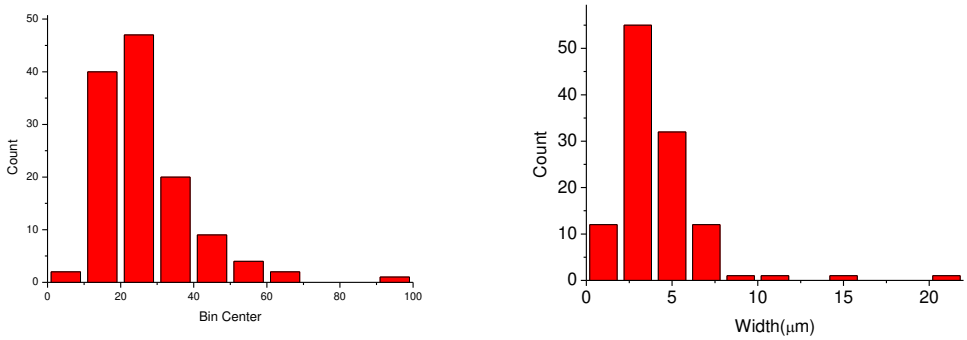

Figure 4.7 Size distributions of Exp14

According to the statistical data based on the size measurements of the material named Exp14, the average length is 32.30 ±14.36 µm and the average width is 4.12 ±2.58 µm. Among the measured crystals, the maximumimum length value was 83.84 µm and the maximumimum width value was 21.46 µm. In the same measurements, the minimum length value is 7.84 µm and the min width value is 1.17 µm (Table 4.6).

Table 4.6 Descriptive statistics on Exp14

	N total	**Mean**	**Standard Deviation**	**Sum**	**Minimum**	**Median**	**Maximum**
Length	121	32.30704	14.35568	3909.1515	7.83709	30.04011	83.83832
Width	115	4.12401	2.57735	474.26103	1.17248	3.69022	21.46251

The size distribution analyses showed that the average length values of the crystals increased and the average width values decreased with the increase in concentration (Table 4.7).

Table 4.7 Effect of reactant concentration on average length and average width

Exp. Code	Reactant Concentration (mol/L)	Average Length (µm)	Average Width (µm)
Exp1	0.04	23.86 ±15.85	5.56 ±3.96
Exp11	0.05	25.21 ±19.63	5.12 ±3.64
Exp12	0.06	26.51 ±12.17	5.57 ±4.70
Exp13	0.07	26.55 ±13.00	4.17 ±2.17
Exp14	0.08	32.35 ±14.36	4.12 ±2.58

4.2 Investigation of PSSS Effect

BET specific surface area analyses used to determine the effect of PSSS additive on crystallization under the aforementioned conditions show that the additive is not effective up to 0.2 g/L concentration (Figure 4.8). Up to this concentration, the BET specific surface area has been measured to be approximately 9 m^2/g.

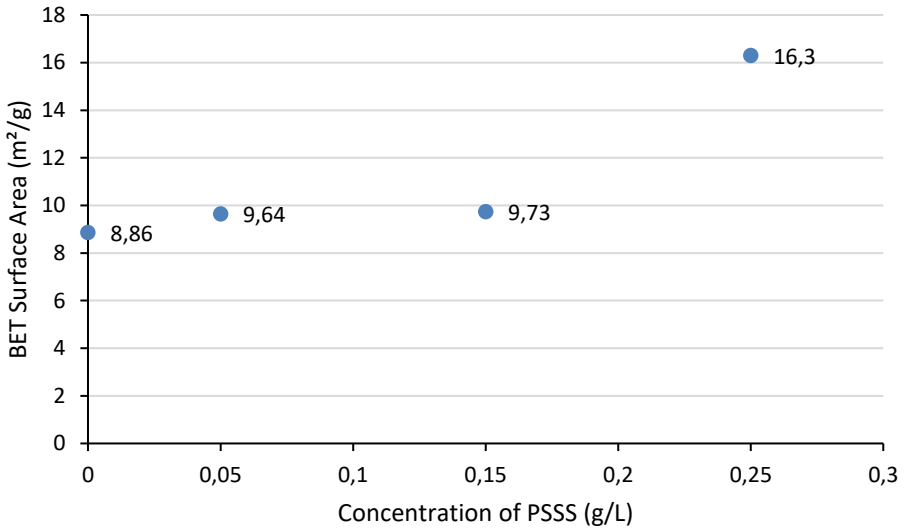

Figure 4.8 Effect of PSSS concentration on BET specific surface area

In the experiment where PSSS additive was used 0.25 g/L, the BET specific surface area value of the produced material was measured as 16.3 g/L.

SEM images of the produced materials are given in Figure 4.9.

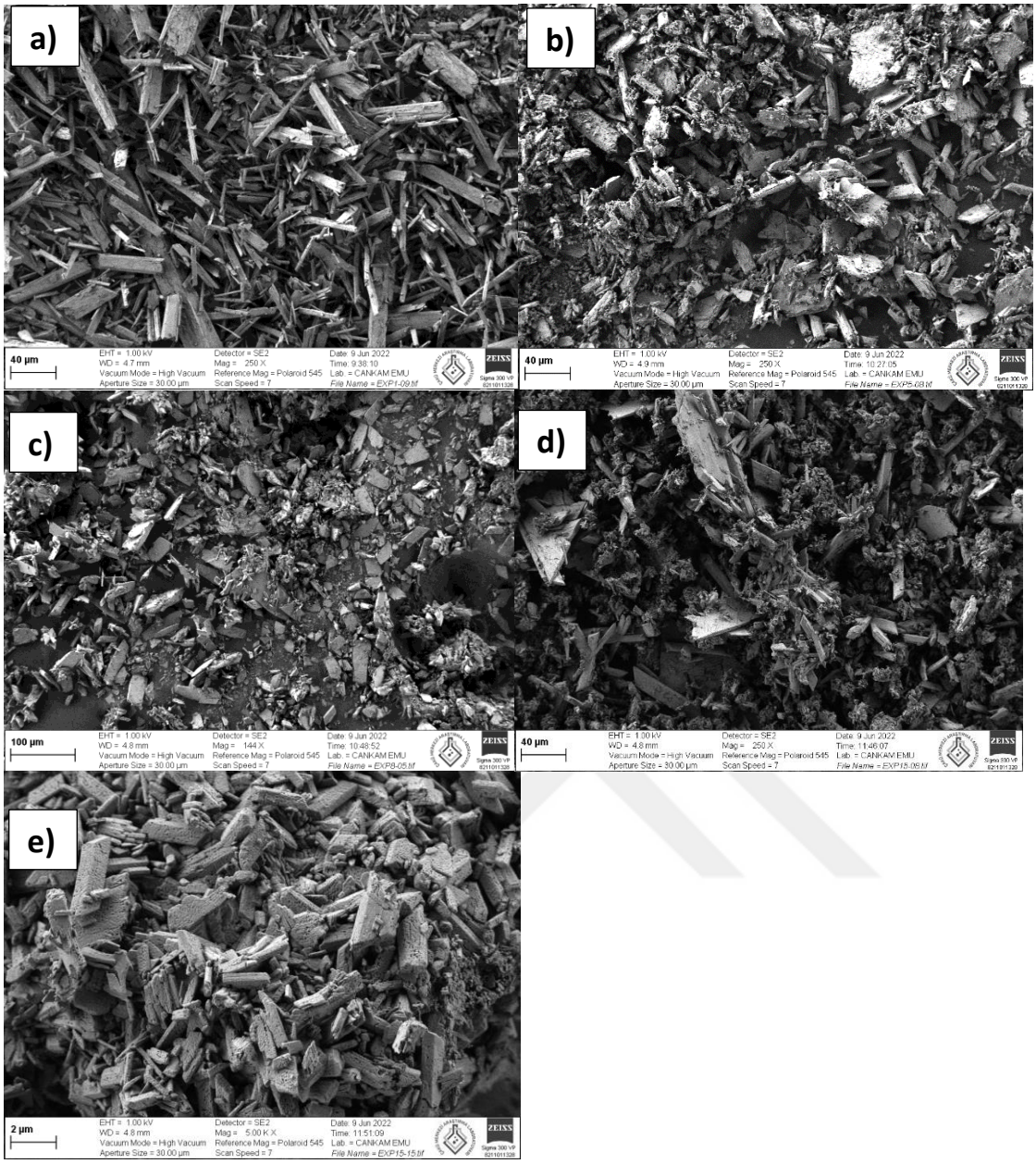

Figure 4.9 SEM micrographs of products under different concentration of PSSS (a) no additive M; (b) 0.01 g/L; (c) 0.15 g/L; (d) 0.25 g/L (250 X); (e) 0.25 g/L (5.00 K X) .

In the experiment performed without additives in SEM images, it is seen that the crystals are rods with smooth surfaces. In the presence of 0.01 g/L additive, the number of crystals with smooth surfaces decreases and this situation continues to increase with increasing concentration. When the SEM images of the material synthesized in the experiment using 0.25 g/L PSSS are investigated with high magnification values, it is

understood that nano-sized crystals occupy more space than micro-sized crystals (Figure 4.9e).

Length and width measurements were made in order to generate frequency histograms from SEM images of the crystals obtained in the experiments in which the effect of PSSS concentration was examined. The length and width distributions obtained in the control experiment without additives are given in Figure 4.10.

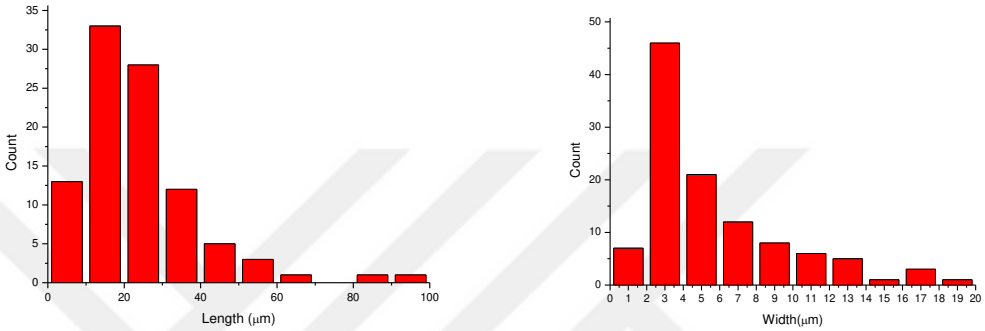

Figure 4.10 Size distributions of Exp1

Table 4.8 summarizes the statistical information of the abtracted control experiment.

Table 4.8 Descriptive statistics on Exp1

	N total	**Mean**	**Standard Deviation**	**Sum**	**Minimum**	**Median**	**Maximum**
Length	97	23.86121	15.85198	2314.53707	2.79299	21.17502	96.97939
Width	110	5.56979	3.95747	612.67734	1.0468	4.16256	19.21182

In Figure 4.11, the length and width distributions obtained in the experiment using 0.05 g/L PSSS are given.

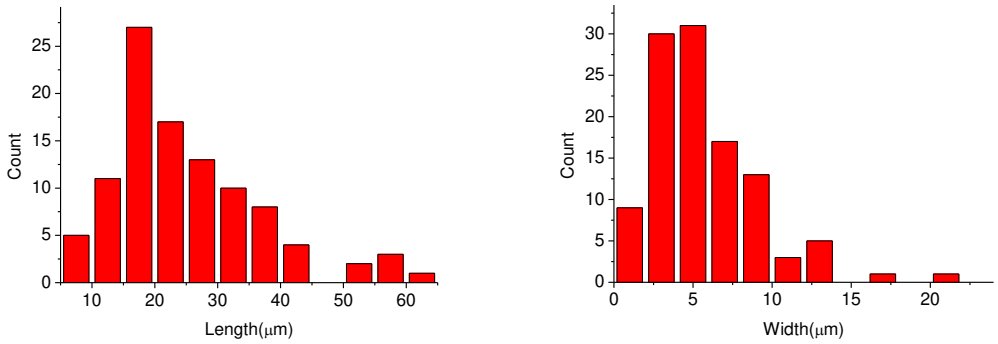

Figure 4.11 Size distributions of Exp5

Statistical information about the experiment performed using 0.05 g/L PSSS is given in Table 4.9. According to these datas, the average height was calculated as 24.85 ±11.57 µm and the average width was calculated as 5.72 ±3.52. µm. The crystal with the maximumimum length value is 63.00 µm and the crystal with the minimum length value is 7.34 µm. The crystal with the maximumimum width value is 21.97 µm and the crystal with the minimum width value is 1.47 µm.

Table 4.9 Descriptive statistics on Exp5

	N total	**Mean**	**Standard Deviation**	**Sum**	**Minimum**	**Median**	**Maximum**
Length	101	24.85466	11.57005	2510.3202	7.3399	21.71182	63.00493
Width	110	5.7247	3.51726	629.71675	1.46552	4.72906	21.97044

The length and width distributions obtained in the experiment using 0.15 g/L PSSS are shown in Figure 4.12.

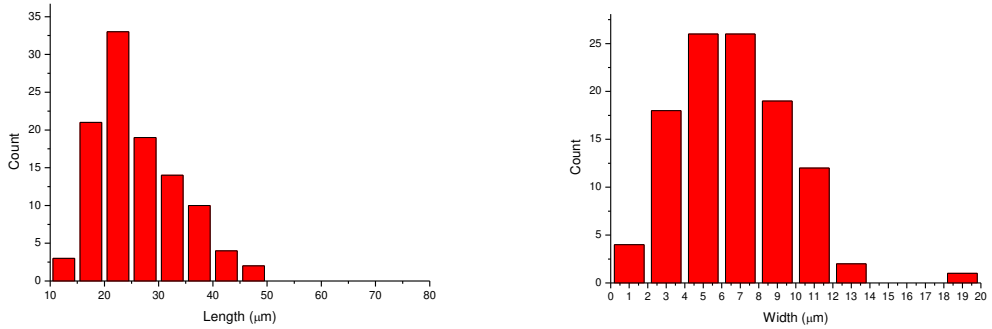

Figure 4.12 Size distributions of Exp8

The statistical information of the material produced in the experiment using 0.15 g/L PSSS is summarized in Table 4.10. The crystal with the maximumimum length value is 46.94 µm and the crystal with the minimum length value is 11.75 µm. The crystal with the maximumimum width value is 18.10 µm and the crystal with the minimum width value is 1.24 µm. According to these data, the average height was calculated as 25.88 ±7.76 µm and the average width was calculated as 6.57 ±3.07 µm.

Table 4.10 Descriptive statistics on Exp8

	N total	**Mean**	**Standard Deviation**	**Sum**	**Minimum**	**Median**	**Maximum**
Length	106	25.87022	7.75887	2742.24324	11.74595	24.21622	46.94054
Width	108	6.57027	3.06596	709.58919	1.24324	6.46486	18.0973

In the experiment using 0.25 g/L PSSS, two different distributions were presented for each size, as a mixture of micro and nano size materials was obtained. The length and width distributions of the obtained micro-sized crystals are given in Figure 4.13.

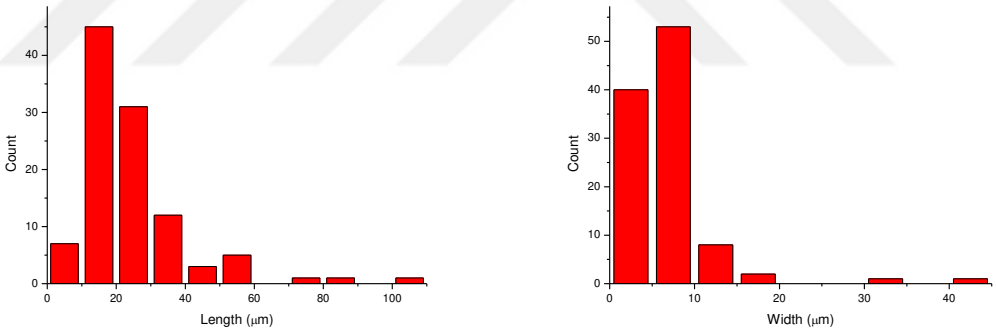

Figure 4.13 Size distributions of micro-sized crystals of Exp15

The descriptive statistics of the material (micro-sized) produced in the experiment using 0.25 g/L PSSS is summarized in Table 4.11.

Table 4.11 Descriptive statistics of mico-sized crystals on Exp15

	N total	**Mean**	**Standard Deviation**	**Sum**	**Minimum**	**Median**	**Maximum**
Length	106	23.91367	15.94304	2534.84946	5.65022	20.84561	105.89366
Width	105	6.84299	5.15412	718.51377	1.67841	5.86803	41.6656

As a result of the measurements made, the crystal with the maximumimum length value is 105.89 µm and the crystal with the minimum length value is 5.65 µm. The crystal with the maximumimum width value is 41.67 µm and the crystal with the minimum width value is 1.68 µm. With these data, the average length value of the micro-sized crystals is 23.91 ±15.94 µm and the average width is 6.84 ±5.15 µm.

In Figure 4.14, the length and width distributions of the nano-sized crystals in the SEM images of the material obtained in the presence of 0.25 g/L PSSS are shown.

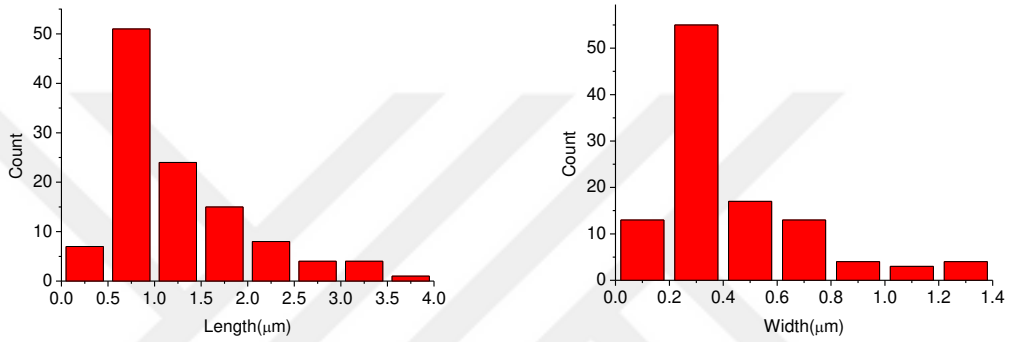

Figure 4.14 Size distributions of nano-sized crystals of Exp15

As a result of the measurements made, the crystal with the maximumimum length value is 3.68 µm and the crystal with the min length value is 344 nm. The crystal with the maximumimum width value is 1.34 µm and the crystal with the minimum width value is 115 nm. According to the SEM analysis of the material, the average length value of the nano-sized crystals was calculated as 1242 736 nm and the average width 439 280 nm (Table 4.12).

Table 4.12 Descriptive statistics of nano-sized crystals on Exp15

	N total	**Mean**	**Standard Deviation**	**Sum**	**Minimum**	**Median**	**Maximum**
Length	114	1.24155	0.73563	141.53717	0.34449	0.99071	3.67534
Width	109	0.43901	0.27973	47.85192	0.11524	0.32776	1.34263

The average length and average width results of the materials produced in the experiments are summerized in Table 4.13. When this table is examined, it is observed

that the average length and average width values do not change with the increase in PSSS concentration. No difference is observed except the formation of nano-sized crystals with increasing concentration.

Table 4.13 Effect of PSSS concentration on average length and average width

Exp. Code	Additive Concentration (g/L)	Micro-sized material		Nano-sized material	
		Average Length (μm)	Average Width (μm)	Average Length (μm)	Average Width (μm)
Exp1	-	23.861	5.569	-	-
Exp5	0.050	24.855	5.725	-	-
Exp8	0.150	25.870	6.570	-	-
Exp15	0.250	23,914	6,843	1.242	0.439

The results obtained in Figure 4.15 wer analyzed graphically. When this graph is investigated, if nano-sized crystals are ignored under operating conditions, the average length value remains the same with increasing concentration, and the average width value rises slightly.

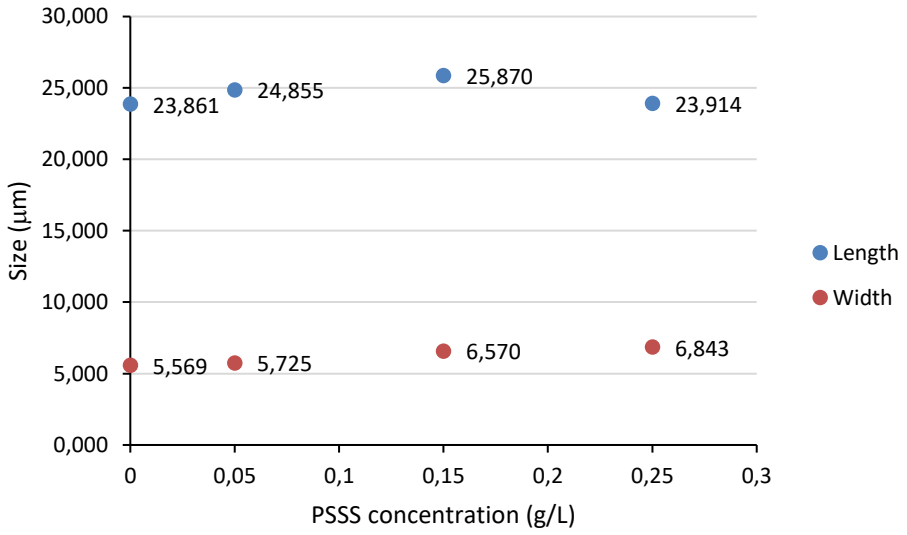

Figure 4.15 Effect of PSSS concentration on average length and average width

5. CONCLUSION AND RECOMMENDATION

In this study, calcium sulfate hemihydrate crystals were synthesized by a rapid reaction using calcium chloride ($CaCl_2$) and sodium sulfate (Na_2SO_4) solutions, and the synthesized crystals were characterized by SEM and XRD. Experiments were carried out at 30 °C, at a stirring speed of 300 rpm. In experiments, reactant solutions were equimolar and kept between 0.04 and 0.08 M values. Analyses of the materials showed that $CaSO_4 \cdot 1/2H_2O$ is obtained. Moreover, a change in crystal size is observed with the increase in the concentration of reactants.

In experiments where the reactants were used at an equimolar concentration of 0.04 M, there was no effect on the mean height and mean width values up to 0.25 g/L PSSS concentration.

When the SEM photographs are investigated, it is understood that the PSSS used as an additive disrupts the crystal order and deforms crystals are obtained.

In experiments performed in the presence of PSSS at a constant equal concentration reactant at 0.04 M, it is seen that the material contains nano-sized crystals when the PSSS concentration reaches 0.25 g/L. At this concentration, the presence of nano-sized material at 16.3 m^2/g is supported by the BET surface area.

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