

MARMARA UNIVERSITY



**INSTITUTE FOR GRADUATE STUDIES IN
PURE AND APPLIED SCIENCES**



**DETERMINATION OF GROWTH AND DISSOLUTION
RATE OF SODIUM PERBORATE TETRAHYDRATE IN
THE PRESENCE OF SILICA IN A FLUIDIZED BED
REACTOR**

DEMET ORHAN

MASTER THESIS

Department of Chemical Engineering

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Prof. Dr. Perviz SAYAN

ISTANBUL, 2015

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ÖZET

AKIŞKAN YATAKLI BİR REAKTÖRDE SİLİS VARLIĞINDA SODYUM PERBORAT TETRAHİDRATIN BÜYÜME VE ÇÖZÜNME HIZININ BELİRLENMESİ

Sodyum perborat tetrahidrat ağartıcı özelliğinden dolayı deterjan üretiminde kullanılır ve sodyum metaborat ile hidrojen peroksitin sulu çözeltilerinden reaksiyonlu kristalizasyon ile elde edilir. Sodyum perborat tetrahidratın fiziksel özellikleri; kristalizasyon koşulları, ortam stokiometrisi ve ortamda bulunan veya ortama sonradan eklenen katkıların etkisi ile değiştirilebilir.

Bu çalışmada sodyum silikat varlığının, sodyum perborat tetrahidrat kristallerinin büyüme ve çözünme hızları üzerindeki etkisi incelenmiştir. Deney sistemi olarak akışkan yataklı kristalizör kullanılmıştır. Deneysel stokiometrik ortamda ve ağırlıkça %2.5 metaborat fazlalığında farklı sodyum silikat konsantrasyonlarında değiştirilerek yürütülmüştür. Deneysel sonuçlarda sodyum perborat tetrahidratın büyüme ve çözünme hızları tespit edilmiştir. Farklı aşırı doygunluk ve doymamışlıkta yürütülen deneyler sonucunda, sodyum perborat tetrahidrat kristallerinin fotoğrafları çekilmiştir.

Stokiometrik ortamda yürütülen deneyler sonucunda; sodyum perborat tetrahidrat kristallerinin çözünme hızı tane boyutundan etkilenmemekle beraber büyüme hızı tane boyutuna bağlı olarak artmıştır. Ayrıca stokiometrik ortamda değişen silis konsantrasyonu büyüme hızını bastırmıştır. %2,5 metaborat varlığında yapılan deneylerin sonucunda sodyum perborat tetrahidrat kristallerinin büyüme hızının bastırıldığı, yüksek silis konsantrasyonlarında bu etkinin daha da arttığı görülmüştür. Elde edilen bütün sonuçlara dayanarak sodyum perborat üretiminin %2,5 metaborat fazlalığında yapılabileceği ve stabilizör olarak silis kullanılmasının olumsuz bir etki yaratmayacağı belirlenmiştir.

Anahtar Kelimeler: Sodyum perborat tetrahidrat, büyüme hızı, çözünme hızı, silis varlığının etkisi, akışkan yataklı kristalizör

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ABSTRACT

DETERMINATION OF GROWTH AND DISSOLUTION RATE OF SODIUM PERBORATE TETRAHYDRATE IN THE PRESENCE OF SILICA IN A FLUIDIZED BED REACTOR

Sodium perborat is used in production of detergents because of its bleaching characteristic and is produced from aqueous solutions of sodium metaborate and hydrogen peroxide via reacted crystallization. The physical features of sodium perborate tetrahydrate can be altered by crystallization conditions, stoichiometri of the media, and the impurities that are present in the media or the impurities that are added to the media.

In this study, the effect of the presence of sodium silicate on the growth and dissolution rates of sodium perborate tetrahydrate. Fluidized bed crystallizer is used as experimental set-up. The experiments are carried out in stoichiometric media and in the presence of %2.5 metaborate excess in the presence of different silica concentrations. The growth and dissolution rates are determined at the end of experiments. The microscopic photographs of sodium perborate crystals are taken for the experiments carried out in stoichiometric media and in the presence of 2.5% NaBO₂.

As a result of the experiments in stoichiometric media, it is seen that although the dissolution rate of sodium perborate tetrahydrate is not affected by the particle size, but the growth rate increases depending on the particle size. Also, the change in silica concentration suppressed the growth rate of sodium perborate tetrahydrate in stoichiometric media. Experiments carried out in the presence of % 2.5 metaborate excess, it is seen that the growth rate of sodium perborate tetrahydrate is suppressed and the effect is higher at high silica concentrations. Considering the results obtained, it can be concluded that the production of sodium perborate tetrahydrate can take place in the presence of 2.5 % metaborate excess and using silica as stabilizer will not create a negative impact.

Keywords: Sodium perborate tetrahydrate, growth rate, dissolution rate, the effect of silica, fluidized bed crystallizer

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LIST OF SYMBOLS

| | | |
|------------------------|--|-------------------------------------|
| A₁ | : Pre-exponential factor | 10^{30} nuclei/cm ³ .s |
| A₂ | : Surface area of the crystal | m ² |
| a_i | : Area of the I th face | m ² |
| c | : Solute concentration in the solution | kg solute/kg solvent |
| c* | : Equilibrium concentration | kg solute/kg solvent |
| c_i | : Solute concentration in the solution at the crystal solution interface | kg solvent/ kg solute |
| D | : Coefficient of diffusion | - |
| g | : Growth rate order | - |
| g_i | : The surface free energy per unit area of the ith face | J/m ² |
| G | : Linear growth rate | m/s |
| ΔG_{cr} | :Critical free energy | J |
| ΔG_s | :Surface free energy | J |
| ΔG_v | :Volume free energy | J |
| K_G | : Overall crystal growth coefficient | - |
| k | : Boltzman constant | J.K ⁻¹ |
| k_d | : a coefficient of mass transfer by diffusion | - |
| k_r | : a rate constant for the surface reaction process | - |
| k_m | : Coefficient of mass transfer | - |
| L | : The characteristic length | μm |
| m₁ | :The amount of crystals put into the crystallizer | g |
| m₂ | :The amount of crystals taken from the crystallizer | g |
| T | :Absolute temperature | K |
| α | : Volume shape sactor | - |
| β | : Area shape factor | - |
| σ | : Surface tension | N/m |

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1.INTRODUCTION

1.1. The Objective of the Study

Sodium perborate is one of the refined products of boron and is produced as a result of the reaction between sodium metaborate and hydrogen peroxide solutions. Because of the bleaching characteristic of detergent production, it is considered one of the important inputs and is produced with different desired physical qualities rather than sodium perborate that are produced in a pure media, and the product characteristics are determined by crystallization conditions, stoichiometry and the effects of additives [1].

The ability of dissolving in water makes it important for being used as bleach in detergents. Sodium perborate solution is not stable at room temperatures and loses its active oxygen in a medium without stabilizer. Hence, adding sodium silicate process creates an impurity effect during crystallization [2].

The presence of impurities in a system has an effect of the growth on product crystal. Impurities might prevent the growth or affect only the crystal surface and as a result change the habit of the crystal. Also, the presence of impurities might have an important effect on the crystal growth. Impurities affect the growth rate of the crystal in two ways. In the first way, the equilibrium of the saturated solution or the properties of the solution is disturbed. In the second way, the characteristics of the adsorption layer in crystal-solution interface are altered. The product properties are affected by these factors. Considering the specific particle size, shape, appearance, bulk density and mechanical resistance of sodium perborate tetrahydrate, the possible effects of impurities are certainly needed to be determined [3].

If in crystal size distribution decreases it results that product crystals to hold main solution at a high amount, which increases the centrifugal force of crystal product at filtration stage. In this stage, additional energy is needed for the crystals that could not be released from the main solution. This results that the quality of the product to decrease and cost of the product to increase. Because of these reasons, it is important to hinder secondary nucleation or to keep it at minimum levels. If there are impurities present in crystallization medium that affects the mechanical resistance of crystals, and as a result of hydrodynamic conditions in a crystallizer secondary nucleation is affected

directly [4]. If the effects of impurities are known, that will make it easier to predict the secondary nucleation to occur in advance, to specify the methods and equipments to be used in order to prevent secondary nucleation.

Based on the above arguments, the purpose of the project is to determine the growth rate and dissolution rate of the crystals by using alkali salts of silica in a fluidized bed system. Hence, it is aimed to understand the impurity effect of the sodium silicate used as product stabilizer on possible effects of product properties.

1.2. Sodium Perborates

The general formula of sodium perborates is represented as $\text{NaBO}_3 \cdot n\text{H}_2\text{O}$ and perborate anion structure is shown in the Figure 1.2.

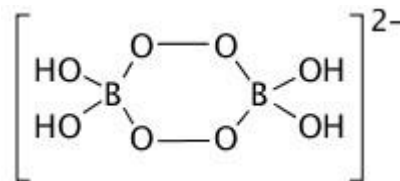


Figure 1. 1. Structure of perborate anion

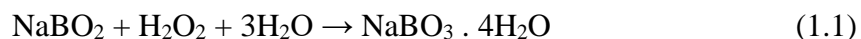
Sodium perborate tetrahydrate consists of 10.4% active oxygen by weight which dissolves in its hydrate water at 63°C degrees as it decays rapidly releasing its active oxygen. Sodium perborate solution is not stable at room temperature.

Sodium perborate monohydrate consists of 16% active oxygen by weight and is acquired from solid tetrahydrate by using different methods.

Sodium perborate trihydrate consists of 11.8% active oxygen by weight. Despite having a higher stability than the stability of tetrahydrate, it is not industrially used. Trihydrate is obtained as a result of tetrahydrate loses its water or in the presence of trihydrate seed crystals crystallizing from the solution that is obtained due to the reaction between hydrogen peroxide metaborate solutions. The crystallization rate is vastly slow compared to tetrahydrate. At temperatures below 15°C, trihydrate converts to tetrahydrate simultaneously [5].

1.2.1. Sodium perborate tetrahydrate

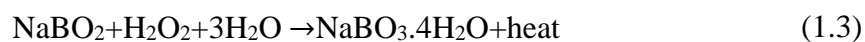
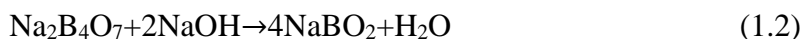
Sodium perborate is a solid peroxygen used as a bleaching agent and is found in washing powders because of its solubility in water. Sodium perborate is generated by the reaction between aqueous solutions of sodium metaborate and hydrogen peroxide which is demonstrated as follows:



The instantaneous redox reaction between hydrogen peroxide and sodium metaborate has a low crystallization rate. The solubility of sodium perborate depends on the presence of the amount of metaborate in the solution [6, 7, 8].

Sodium perborate tetrahydrate can be produced chemically and electrochemically. Due to its economical benefits and efficiency, the chemical method is preferred more in the industry. Production of sodium perborate tetrahydrate from metaborate is the most common chemical method used in the industry.

The fundamental basis of this method is to prepare metaborate solution previously and to react it with hydrogen peroxide. Sodium perborate tetrahydrate is crystallized from the solution and the reaction steps are shown as follows:



Borax and solid sodium hydroxide are used in this method. Borax can be either pentahydrate or decahydrate. In the second step of this method, metaborate solution is reacted with hydrogen peroxide solution. For this reason; sodium perborate tetrahydrate, which is more stable than hydrogen peroxide and less soluble than sodium metaborate, is produced with an exothermic reaction and is crystallized from the solution [5, 9].

If the concentration is lower than 2 g/l, the equilibrium gets on the side of hydrolysis and to the side of products while the concentration is higher than 12 g/l; the

undissociated molecule exists in aqueous solutions. The degradation of hydrogen peroxide to active oxygen and water causes an irreversible shift of the equilibrium [10].



This reaction is the fundamental of the bleaching effect of the sodium perborate. In order to use sodium perborate tetrahydrate in detergents, two methods are followed. It can be used directly or can be converted to monohydrate by using the latest technology. In order not to cause breakage, the strength of the crystals should be increased. If the crystal growth habit and the size can be modified, the strength of the crystals will be changed. Crystal strength is arranged by changing the process conditions such as excess of one of the reactants or additives [11].

1.2.2. Previous studies on sodium perborate tetrahydrate

Reactans and productions methods can be altered in order to obtain sodium perborate tetrahydrate with desired qualities. Also, the impurities which are present in the medium initially or are added can change the quality of sodium perborate tetrahydrate directly. A number of operations are applied during crystallization to change the physical properties of the product.

One of the methods applied in order to change the properties of produced sodium perborate is to change the ratio of reactants and to have excess of one of the reactants in the medium. According to a study that was performed by taking this principal into account, the crystals showed prismatic form in stoichiometric media, spherical form in the presence of free metaborate and branched quadruplet form in the excess of hydrogen peroxide. Also the smaller the reactant concentration the larger the crystal size is [5].

In another study that was carried out, the crystallization of sodium perborate was analyzed and was observed that the excess of metaborate was necessary because it increased the average particle size of the product. Considering the factors that determine the product quality such as average particle size, particle shape and distribution, the optimum condition for crystallization is the solution containing 27 g/l sodium metaborate and 5 g/l borax and the pH is kept at 10.40.

Along with changing the reactant ratio, the additives can alter the physical properties of sodium perborate. In a study about this, the presence of ethyl, butyl isopropyl alcohol, butyl or isopropyl resulted in obtaining spherical crystals with high mechanical resistance [5].

Nucleation and growth rate are two factors that determine the product size distribution. Thus, the factors that affect the properties of sodium perborate also affect nucleation and growth rate directly. In a study that was carried out by Chianese, the solubility of sodium perborate tetrahydrate was measured in stoichiometric media and excess of sodium metaborate at 20°C and 25 °C. Also the waiting time was measured as a function of supersaturation of sodium perborate in stoichiometric media and in the presence of 4.5% NaBO₂. The results showed that the solubility of sodium perborate decreased until 2% of NaBO₂ presence for both temperatures and then increased [5].

In another study, the solubility of sodium perborate was measured in water and in solutions containing sodium metaborate for ten different temperature values. As a result of this study, the solubility curve showed the same tendency for each temperature.

Nucleation rate measurements of sodium perborate in stoichiometric media, metaborate excess media, in the presence of hydrogen peroxide excess, sodium metaborate excess and borax being present in the same media were carried out. The experiments showed that the nucleation rate increased due to the presence of borax and hydrogen peroxide. If the excess of sodium metaborate is above 30 g/l sodium perborate tetrahydrate had the optimum crystallization condition considering the nucleation rate constant, rate order and metastabil zone width [5].

The dissolution and growth rate of sodium perborate were measured in a fluidized bed crystallizer and using a rotary disc apparatus. Similar results were obtained for each system, the total growth rate was found to be first order.

In another study in which the effect of sodium metaborate, temperature, crystal size and shape on the growth and dissolution rates of sodium perborate in a fluidized bed reactor were examined. The result of this study showed that there was no significant difference on the dissolution and growth rate of the crystals with regular and dendritic structure. As the metaborate concentration increased the growth rate decreased. This is very

significant at 4.7% NaBO₂ concentration. Also temperature increased the growth rate but did not cause any change on the dissolution rate [5].

In order to stabilize sodium perborate products, magnesium sulphate and sodium silicate can be added to the reaction medium to obtain magnesium silicate. The concentration of magnesium silicate and the ratios of the substances affect the crystallization process as well as the product quality.

In another study that was carried out, the effect of silica for two different metaborate concentration and waiting time were observed. Keeping the metaborate concentration as maximum as possible and the silica concentration at 100-200 ppm affected crystallization positively [5].

The factors of primary and secondary processes such as nucleation, growth and agglomeration affect the quality of the product. Chianese et al. showed the determination of the nucleation rate by measuring the metastable zone width. On the other hand David, Bossoutrot, Pohar and Livk estimated the kinetic parameters of nucleation by using a method for simultaneous parameter specification [9].

Along with solubility, crystal growth has also been studied by different scientists such as Söhnel et al., Chianese et al., and Frances et al. who showed that the crystal growth rate was size-independent and they found different growth rate laws [9].

In a study that was carried out the solubilities of sodium perborate tetrahydrate were investigated. In order to measure the crystal growth and metastable zone width, the solubilities of sodium perborate tetrahydrate should be known. In order to determine the supersaturation level, the solubility values are one of the factors that are used. The results showed that the solubility of sodium perborate decreased when the sodium metaborate concentration was less than between 1-2 mass %. If the sodium metaborate concentration was between 2-3% mass, the effect on the sodium perborate concentration was slight [11].

1.3. Crystallization

Crystallization is a separation method that is used to decrease the concentration of a substance which is not desirable in a solution or to separate a crystallized product from

impure solutions. Crystallization is one of the the most important processes which is used for purification, separation and acquiring crystals with quality. After crystallization process, the obtained crystals are pure, good and suitable to process [12, 13].

A production method is the necessity for the chemical and physical features of a product that is considered for crystallization. The characteristic features define microscopic characterization of crystals such as size and shape.

Crystallization process purifies liquids as a result of forming crystals. As well as a separation method, it is also a particle formation process by which molecules in solution or vapor are turned into solid phase. Larger particles are tend to separate from fluids more quickly than fine ones and are more prone to dust formation while smaller particles dissolve faster [14].

Crystallization process consists of nucleation and crystal growth and a change of free energy is required. Nucleation and crystal growth depend on supersaturation degree. Supersaturation can be defined as the difference between the actual and equilibrium concentrations and is a driving force for crystallization to occur. Supersaturation state consists of more dissolved solid in the solution than the equilibrium conditions [12, 15].

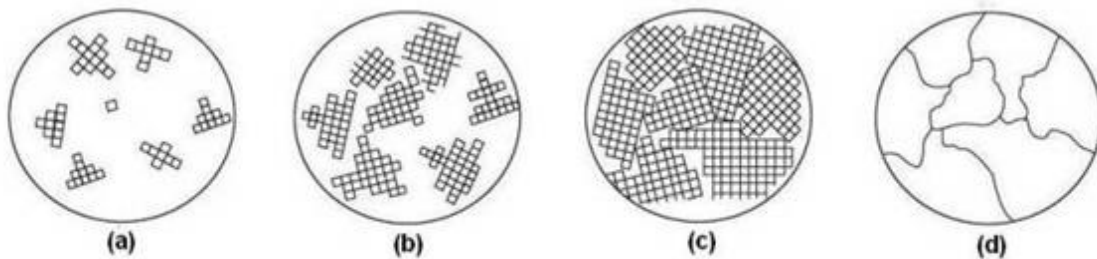


Figure 1.2. Schematic representation of crystallization

- (a) Spontaneous appearance of nuclei at various points in the liquid
- (b) Growth of nucleus (crystal)
- (c) Mutually obstruction in dendrites
- (d) Grains and grain boundaries as seen in a microscope

Along with supercooling and supersaturation in a system to start crystallization, it is also needed to have a number of solid bodies, nuclei or seeds in the solution in order to

develop crystals. Nucleation takes place spontaneously or is started externally. Agitation, mechanical shock, friction and extreme pressures in the solution are some of the fundamental stimulants used for nucleation process to take place [16].

Crystallization is used for pharmaceuticals, zeolites, catalysts, proteins and food products as well as biotechnology, mineral processing, waste treatment and new construction materials. Crystal size distribution is very important for designing industrial crystallizers because of the need of each crystal to be strong, uniform and non-cumulative [17].

1.3.1. Solution, solubility and supersaturation

A solution is a mixture that consists of two or more substances to form a homogenous phase. Solubility is the amount of solute needed for obtaining a saturated solution. The solubility of a substance in a solvent can be defined as the maximum concentration that exists at equilibrium at a given temperature. Solubility mostly increases with the temperature of the solution [18].

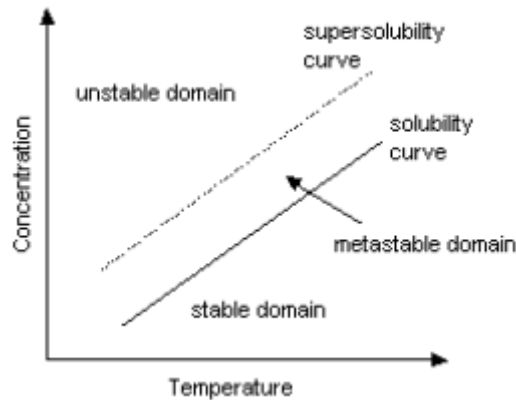


Figure 1.3. Solubility-supersolubility diagram

1. Undersaturated (stable): crystals present will dissolve, there is no crystallization
2. Metastable: a supersaturated region in which crystals will grow, but spontaneous crystallization is unlikely.
3. Labile: a region in which a solution will nucleate spontaneously

The time needed for crystallization depends on driving force which is called supersaturation. In order to achieve supersaturation, changing the temperature also known as cooling is one of the common methods as well as other methods such as evaporation of solvent, chemical reaction, and changing the solvent composition.

The separation or the formation of new crystals is the first step of crystallization which is called nucleation. The second step is the growth of these crystals to larger sizes which is called crystal growth. In order for a solution to crystallize, the supersaturation needs to be relieved. A metastable zone takes place in supersaturated solutions and the occurrence of nucleation is not inherent. If the level of supersaturation is raised sufficiently, nucleation will take place spontaneously at an increased supersaturation. This is defined as metastable limit.

1.4. Nucleation

Nucleation is the beginning of formation of a new crystal. It is stated that when the solution is supersaturated, the molecules begin to merge and cause the formation of clusters or concentration fluctuations. Nucleation is a first order phase transition mechanism. It is the process of creating a new phase with a lower free energy than the old phase. In a large volume of the old phase, nucleation occurs through the generation of small embryos of the new phase [18, 19, 20].

Nuclei grow to form crystals. Nucleation is first step of formation of the solid occurs as a result of clustering and aggregation of molecules or ions in a supersaturated melt, solution or vapor [21].

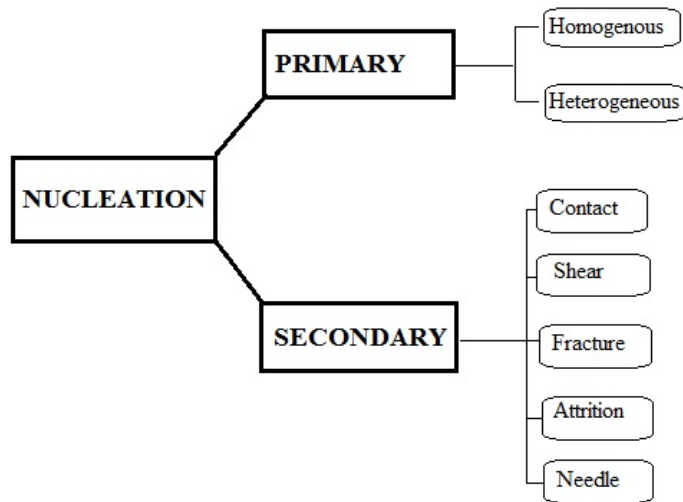


Figure 1.4. Modes of nucleation mechanism

Nucleation can be separated into two groups:

- Primary nucleation (nucleation without crystalline matter)
 - Homogenous nucleation(spontaneous nucleation from clear solution)
 - Heterogeneous nucleation(induced by foreign particles)
- Secondary nucleation(induced by presence of existing crystals)
 - Contact(with other crystals or the crystallizer parts)
 - Shear(due to fluid flow)
 - Fracture(due to particle impact)
 - Attrition(due to particle impact or fluid flow)
 - Needle (due to particle disruption)

Homogenous nucleation occurs if a solution does not contain foreign solid particle and its own crystals. If foreign particles are present in the solution the process is called heterogeneous nucleation. Primary nucleation is defined as the absence of solution-own kind of crystals in the solution in both homogenous and heterogeneous nucleation [16].

Primary nucleation generally occurs at high level of supersaturation. The rate of primary nucleation is subject to factors such as diffusivity D_{AB} , the solubility c^* , the density c_c of the crystals and the supersaturation S [14, 18].

1.4.1. Homogenous nucleation

Homogenous nucleation starts with the generation of stable nuclei. In a supersaturated solution, which does not hold equilibrium state, the average concentration of the solution is a stable value at a specified temperature. But, the fluctuations in local concentrations can result in increase to clusters. It is assumed that clusters are produced by an addition technique [18, 21].

$$a + a = a_2 \quad (1.5)$$

$$a_2 + a = a_3 \quad (1.6)$$

.....

$$a_{c-m} + a_m = a_c \quad (1.7)$$

The rate of nucleus generation is shown by the Arrhenius type of expression in Equation 1.8.

$$B_0 = A_1 \exp\left(-\frac{\Delta G_{cr}}{kT}\right) \quad (1.8)$$

where,

A_1 is pre-exponential factor, k is the Boltzman constant, ΔG_{cr} is critical free energy and T is absolute temperature.

Adding the free energy variation for generating the nucleus surface to the free energy variation for changing the phase gives the free energy variation for the new phase [21].

$$\Delta G = \Delta G_s + \Delta G_v = \beta L^2 \sigma + \alpha L^3 \Delta G_v \quad (1.9)$$

Figure 1.5 shows the free energy variations and their sum for a spherical nucleus. From the figure it can be concluded that a decrease in free energy is caused by clusters which are greater than critical size and that leads in the nucleation process. In order to obtain the critical size, the free energy function relating to the radius should be minimized.

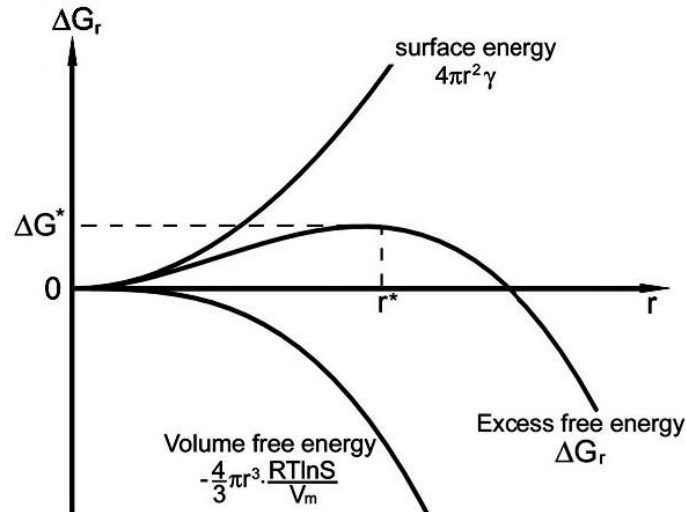


Figure 1.5. Free energy diagram

For a system to nucleate; there is an optimum temperature and values below the optimum temperature decreases the tendency of nucleation. If the system is free from the impurities, there is a difficulty related to the impurities acting as nucleation catalysts and the removal of the effects of retaining container walls that often eases nucleation. In order to stimulate crystallization, agitation is used. It has been observed that the solutions that are agitated nucleate spontaneously at lower degrees of super cooling than the solutions that are not agitated [17].

1.4.2. Heterogeneous nucleation

Heterogeneous nucleation occurs due to the presence of foreign nuclei in the solution and it becomes significant at lower supersaturation levels. The energy that is needed for nucleation is lowered by the presence of foreign substance in a supersaturated solution. For a heterogeneous system, nucleation generally takes place at a lower supersaturation than for a homogenous system as a result of the lower free energy barrier [18, 21].

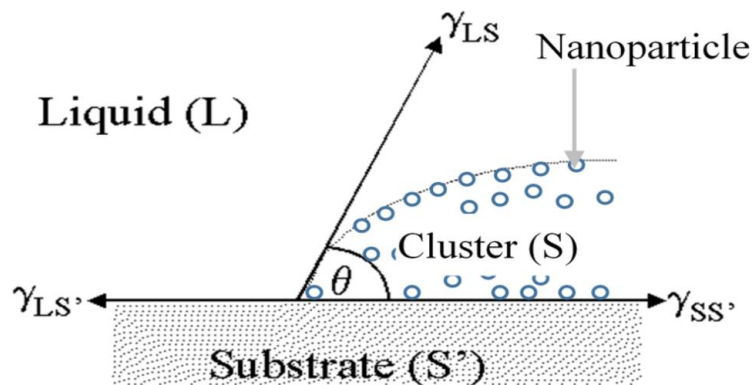


Figure 1.6. Surface energies in heterogeneous nucleation

Volmer showed that the decrease in free energy was linked to the contact angle of the solid phase. Hence in order nucleation to occur in a heterogeneous system, the supersaturation level needs to be lower. Nucleation occurs spontaneously if the contact angle is zero. But there is no such a system in practice. Impurities in a system affect the rate of nucleation of a solution. An impurity which is acting as a nucleation inhibitor does not mean it will be effective in another system [17, 21].

1.4.3. Secondary nucleation

Secondary nucleation occurs due to the crystals which are present in the supersaturated solution. There are several theories explaining secondary nucleation as follows;

- initial or dust breeding
- needle breeding
- collision breeding

In initial breeding or dust breeding, the seed crystals cause the secondary nucleation. The growth of seed crystals process consists of formation of tiny crystallites on the crystal surfaces. The crystallites act as nucleation sites in the solution which are larger than the critical size. As a result of this, the nucleation does not depend on the supersaturation of the solution or the stirring rate [21].

In needle breeding, needle-like or dendritic crystals are produced at high levels of supersaturation. In the solution, the crystals are present as nucleation sites. At high levels of supersaturation, disorganized polycrystalline aggregates are produced and act

as nucleation sites and this is defined as polycrystalline breeding. The polycrystalline breeding is not preferred in the industry. At accelerated stirring levels, crystal abrasion occurs and acts as nucleation sites. This is called collision or attrition breeding and the rate of nucleation is related to the crystal hardness, the concentration of the suspension and the detention time [21].

Three steps affect the rate of secondary nucleation. These are:

- Secondary nuclei is generated
- The clusters are removed
- Crystals are grown in order to form a new solid phase

1.4.4. Contact nucleation

As a result of collision in a liquid medium, complex behaviours can be promoted. Fracture may take place at the contact point. But due to hydrodynamic forces over the surfaces around the point of contact, plastic and elastic deformation in the parent crystal is increased. As a result of energy absorption, a small portion ruptured by collision could be in a disordered state with dislocations and incompatible surfaces. Thus, small crystallines grow slowly than macrocrystals. Also the contact between the crystal and the agitator are the main suspected factor for the secondary nucleation. These crystals are able to pass through the fluid boundary layer around the blade. The possibility of a hit is directly proportional to the rotational speed of the agitator. Also the material of the impeller has an effect on nucleation rate [17].

1.5 Crystal Growth

Crystal engineering is one of the main necessities in materials in order to be able to control properties such as crystal perfection, crystal size, intergrowths, chirality and cost [19].

Crystal growth is the combination of diffusion and integration processes, and is altered by the effect of the solid surfaces. Firstly, solute molecules or ions arrive at the growing surfaces of a crystal via liquid phase. Then the molecules or ions organize themselves via an adsorbed layer at the surface [18].

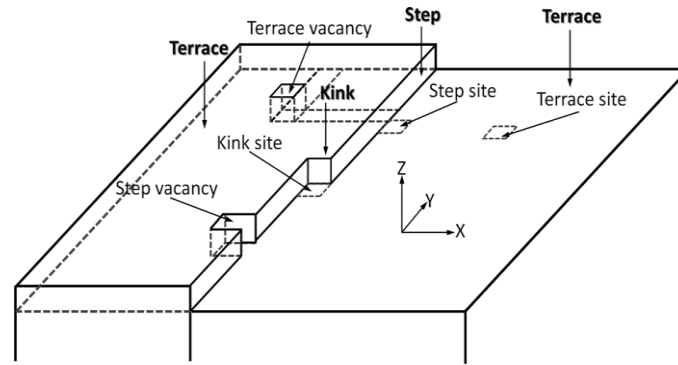


Figure 1.7. Structure of a crystal surface

Crystal growth is the series of processes which cause an atom or a molecule to increase its size.

- atoms are transferred via solution;
- atoms are attached to the surface;
- atoms are moved on the surface;
- atoms are attached to edges and kinks [19].

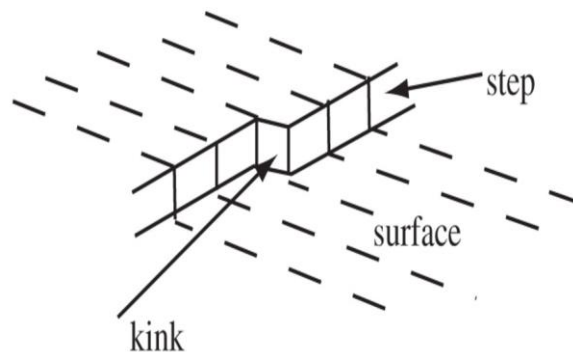


Figure1.8.Schematic representation of a kink

The attachment process of molecules to a step-edge does not include energy cost as well as adding a molecule at the kink effectively. If the step consists of kinks, during the addition of a molecule to a kink, the kink is shifted alongside the step [22].

The basis of crystal growth process is mass transport to the crystal surface from the solution via diffusion, convection or both mechanisms.

The second part can be divided into several stages:

- The growth unit adsorption
- Releasing the part salvation shell which is followed by diffusion of the growth unit into the adsorption layer.
- Arrival of the growth unit to a point into the lattice

Crystal growth and nucleation have the control on the particle size distribution acquired in the system. The conditions in the system and the growth rate influence the product purity and the crystal habit are controlled by conditions and rate of crystal growth [18, 21].

1.5.1. Crystal growth theories

Crystals start to grow in a supersaturated solution or supercooled system, when the stable nuclei particles becomes larger than critical size. The diffusion theories propose that, matter is established continually on a crystal face. And the rate is related to the difference between the concentration of deposition point and the concentration of the bulk solution. Volmer proposed that the crystal growth was taking place by adsorption on the surface of the crystal [17].

1.5.2. Surface energy theories

If the surface energy and the area of a droplet of a fluid is minimum, then the droplet is said to be most stable. Gibbs proposed that the crystals grow as if they will have the minimum surface energy [5, 17].

Assuming that the volume free energy per unit volume is constant;

$$\sum_1^n a_i g_i = \text{minimum} \quad (1.10)$$

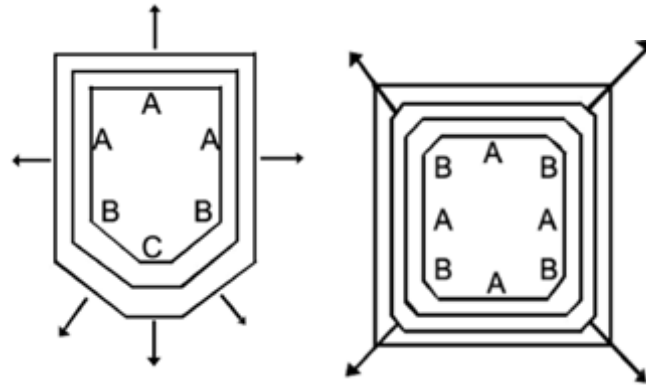


Figure1.9: Velocities of crystal growth faces

When a crystal grows in a supersaturated medium, it develops an equilibrium shape ensuring that the crystal has a minimum total free energy for a specified volume. Wulff demonstrated that the equilibrium shape depends on the free energies of the faces and the rate of a crystal to grow is related to the surface energies [17].

Because of the limited findings on surface energy theories, there is not a common acceptance. Although these theories attract attention of the scientists, the main issue is the failure of explaining the known effects of supersaturation and solution growth on the crystal growth rate [17].

1.5.3. Adsorption layer theories

Volmer proposed that crystal growth took place in the presence of an adsorbed layer of solute atoms or molecules. When the crystallizing units reach to the crystal face, the integration into the lattice does not start immediately. After losing the degree of freedom, the units are able to emigrate over the crystal face. Thus, there is a loose adsorbed layer, which brings units together at the interface and equilibrium is obtained between this layer and the bulk solution.

The linking of atoms and molecules into the lattice will occur where the attractive forces are greatest at the active centers. A center of crystallization appears on the plane surface before the crystal face is able to grow [17].

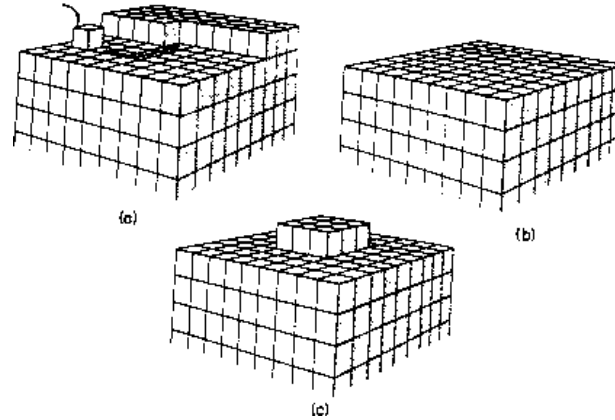


Figure 1.10: A mode of crystal growth without dislocations

1.5.4. Diffusion-reaction theories

Noyes and Whitney assumed that the reverse of dissolution was crystallization and the difference between concentration at the solid surface and in the bulk of the solution was used to determine the rate of both processes [17].

$$\left(\frac{dm}{dt}\right) = k_m A_2 (c - c^*) \quad (1.11)$$

The assumption of existence of a thin stagnant film of liquid adjacent to the crystal growing face is made and the equation becomes:

$$\left(\frac{dm}{dt}\right) = \left(\frac{D}{\delta}\right) A_2 (c - c^*) \quad (1.12)$$

The thickness is affected by the relative solid-liquid velocity. In agitated systems, film thickness values on stationary crystals in stagnant aqueous solutions drop to zero. This means that in agitated systems there is an almost infinite rate of growth. In this case, crystallization is not necessarily considered as reverse dissolution.

The mass deposition consisted of two steps. Berthaud and Valetton suggested that the solute molecules were transported from the bulk of the fluid phase to the solid phase in a diffusion process which is followed by a first order reaction.

$$\left(\frac{dm}{dt}\right) = k_d A_2 (c_1 - c_i) \quad (\text{diffusion}) \quad (1.13)$$

$$\left(\frac{dm}{dt}\right) = k_r A_2 (c_1 - c^*) \quad (\text{reaction}) \quad (1.14)$$

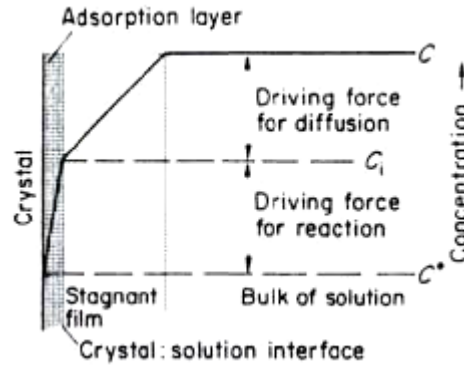


Figure 1.11. Driving forces of crystallization from solution

Applying Equation 1.13 and 1.14 in practice has difficulties because interfacial concentrations are involved, which are not easy to determine. A general equation can be written as;

$$\left(\frac{dm}{dt}\right) = K_G A_2 (c_1 - c^*)^g \quad (1.15)$$

where;

K_G is overall crystal growth coefficient, A_2 is surface area of the crystal, c^* is the solute concentration in the solution and g is growth rate order.

The exponent g is the reaction order of the process. If $g=1$ and the surface reaction is first order. The interfacial concentration can be eliminated and the equation can be rewritten as;

$$\left(\frac{dm}{dt}\right) = \frac{A(c - c^*)}{1/k_d + 1/k_r} \quad (1.16)$$

$$\frac{1}{K_G} = \frac{1}{k_d} + \frac{1}{k_r} \quad (1.17)$$

$$K_G = \frac{k_r k_d}{k_r + k_d} \quad (1.18)$$

where,

k_d and k_r are coefficient of mass transfer by diffusion and rate constant for the surface reaction process respectively.

For large k_r values, the crystallization process is said to be diffusion controlled and for large k_d value, the process is said to be surface integration controlled.

1.6. Effect of Impurities and Additives on Crystallization

An impurity is any substance in a system that is not being crystallized. Impurities are important because the morphology, shape, quality, growth and dissolution rates of crystals are affected by the presence of impurities in a system [23].

1.6.1. Effect of impurities on nucleation

The presence of impurities in a system affects nucleation. If impurities are adsorbed by crystal nuclei, the supersaturation level increases. As a result of this, the metastable zone increases. An increase in the insoluble impurity concentration causes a decrease in the metastable zone width [24].

Nucleation inhibiting effect increases with the increasing ionic charge at cationic substances. Also, it is suggested that the presence of impurities suppressed the primary nucleation and when the uptake of impurity is significant secondary nucleation occurs [3, 13].

Another effect of impurities on nucleation is the solubility thus supersaturation level change. If the impurities increase the supersaturation level, the nucleation rate will increase as well [25].

1.6.2. Effect of impurities on crystal growth

The existence of impurities in a system might have an effect on crystal growth. Impurities might prevent growth completely, increase growth or affect only certain

crystallographic faces. Hence the presence of impurities modifies the crystal habit. Some impurities can apply an effect at very low concentrations less than 1 ppm while other impurities need to have large amount in order to demonstrate any effect. Impurities affect the crystal growth in number of ways. They can change the solution properties or the equilibrium saturation concentration hence the supersaturation. Also impurities modify the characteristics of the adsorption layer at the crystal-solution interface [17].

pH is an important factor which affect crystallization and crystal growth. For this reason some studies are focused on changing the pH of a system in order to observe the effect on nucleation and crystal growth. It was seen that the neutral solutions has maximum growth rate than acidic or alkaline solutions [23].

The presence of Cr^{3+} , Fe^{3+} and Al^{3+} ions affects the pH of a solution which changes the crystal habit. In a study it was found that the presence of ferrous ions in a solution did not have any effect on the growth rate of calcium carbonate between pH values of 7 and 8 [23].

1.6.3. Effect of impurities on crystal habit modification

Crystal habit is important in order to define the easiness and effectiveness of solid/liquid separation, bulk density, breakage and dustiness. The relative rates of growth of a crystal, is a factor for determining the overall shape of a growing crystal. If the growth rate is smaller, the face becomes larger. The parameters that control the growth rate of a surface are intermolecular bonds and dislocations, supersaturation, temperature and impurity concentration [13].

2. EXPERIMENTAL PROCEDURE AND ITS THEORY

2.1. Growth Rate Measurement Techniques in Fluidized Bed Reactors

Fluidized bed reactors are preferred because of being the closest to the real crystallizer conditions and the growth rate measurements are performed by using two methods proposed by Mullin. These methods are differential and integral methods. These methods are used to measure the growth rates of crystals in fluidized bed crystallizer.

2.1.1 Integral method

It is faster than differential method. It is based on determining the concentration change during the experiment. Thus, with one experiment, growth rate can be measured at different supersaturation levels. But the concentration change cannot be measured precisely and consisting of many parameters which are far from being computable makes this method difficult to use [5].

2.1.2. Differential method

The differential method is based on adding a known amount of crystals with a known sieve fraction to the system. The crystals start to grow in a supersaturated solution. Due to adding small amount of crystals to the system it is assumed that the concentration of the solution does not change during the growth process. According to differential method it is also assumed that

- there is no nucleation in the system.
- the number of crystals which are put in the growth cell and taken from the growth cell are equal,
- all crystals are at the same size and have the same volume shape factor and
- all crystals grow and dissolve in the same proportion when measuring the growth rate because there is no growth dispersion [5, 26, 27].

The amount of crystals added to the crystallizer is m_1 and the amount of crystals taken from the crystallizer is m_2 and the size of the crystals is L . Then the amounts of crystals can be written as a function of L [26].

$$m_1 = \alpha \rho L_1^3 \quad (2.1)$$

$$m_2 = \alpha \rho L_2^3 \quad (2.2)$$

The overall linear growth rate can be determined by the rate of change of characteristic size;

$$G = \frac{\Delta L}{t} \quad (2.3)$$

The growth rate can be determined in terms of size of the seed crystals and the weight of the crystals by combining Equations 2.2 and 2.3

$$G = \frac{L_1}{t} \left[\left(\frac{m_2}{m_1} \right)^{1/3} - 1 \right] \quad (2.4)$$

2.2. Experimental Set-up

The experimental set-up was shown in Figure 2.1, consisting of a fluidized bed crystallizer. The apparatus consisted of a 20 L of storage tank, and the solution in the storage tank was kept circulated by a centrifugal pump. The fluidization cell that was used is 200 mm height with a 12 mm of inner diameter. The bottom and top parts of the cell was covered by sieve wire to prevent the loss of crystals that are placed inside the cell. For each experiment, 2,5g \pm 10 mg pure sodium perborate tetrahydrate with the sieve fraction which is going to be examined was placed and the experiments were carried out.

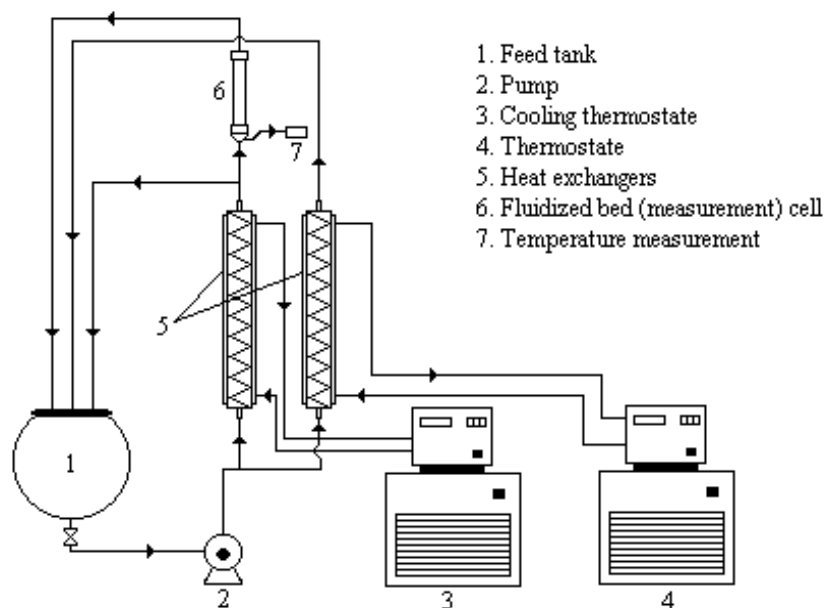


Figure 2.1 Experimental set-up

The supersaturation that was needed for the experiment was provided by a heat exchanger changing the temperature of the solution passed through the cell below the saturation temperature. In order to prevent nucleation occurrence in the system, the temperature of the solution in the storage unit is kept above saturation temperature by a thermostat with a constant temperature. Each experiment was carried out 12 minutes and the temperature is measured at one minute intervals. The average temperatures were used for calculating the growth rate.

Sodium perborate solutions having any desired level of sodium metaborate used in the experiments were prepared from H_2O_2 (15% w/w) and sodium metaborate (10% w/w) solutions prepared by dissolving pure metaborate tetrahydrate crystals. 30% (w/w) H_2O_2 was diluted to 15% (w/w) with distilled water before being used. Pure sodium metaborate tetrahydrate was prepared by the reaction of borax decahydrate and sodium hydroxide in hot solution. Sodium carbonate was added to precipitate alkaline earth metals in the solution. The filtered solution was crystallized to give $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$. The crystals were washed and dissolved at high temperature, then filtered from a membrane filter and then re-crystallized. Concentrations of sodium perborate solutions which were prepared from NaBO_2 and H_2O_2 solutions were determined by titration of boron and active oxygen content of the solutions and controlled by the determination of alkalinity content.

Experiments were carried out at stoichiometric, and 2.5% free sodium metaborate media. Desired silica concentration was maintained by adding sodium silicate solution into sodium perborate solution. Seed crystals were in $-425+355 \mu\text{m}$ and $355+250 \mu\text{m}$ particle size range. Desired supersaturation (or undersaturation) level was obtained by adjusting the temperature of solution passing through the measuring cell. During the experiments, the temperature in the cell was measured by Pt-100 thermo element connected to a digital thermometer and kept between $\pm 0.1^\circ\text{C}$. At the end of the each experiment, the crystals which were taken from the cell filtered, air dried and weighed.

The growth or dissolution rate was calculated by using Equation 2.4:

$$G = \frac{L_1}{t} \left[\left(\frac{m_1}{m_2} \right)^{1/3} - 1 \right] \quad (2.4)$$

Growth and dissolution rate values obtained from this equation for each temperature using equation 2.4. The saturation temperature of sodium perborate solution was taken as the temperature which the growth and dissolution rate value is zero in this diagram.

3. RESULTS AND DISCUSSIONS

The growth and dissolution rates of sodium perborate tetrahydrate crystals for both in pure sodium perborate solutions and sodium perborate solutions in the presence of 2.5% (w/w) metaborate concentration are determined. Furthermore, effect of five different silica concentrations on the growth and dissolution rate of sodium perborate tetrahydrate crystals is investigated in both media.

The experiments which were carried out in stoichiometric media, Merck sodium perborate tetrahydrate crystals with particle size of $-425+355 \mu\text{m}$ and $-355+250 \mu\text{m}$ were used. The results obtained are shown in Figure 3.1.

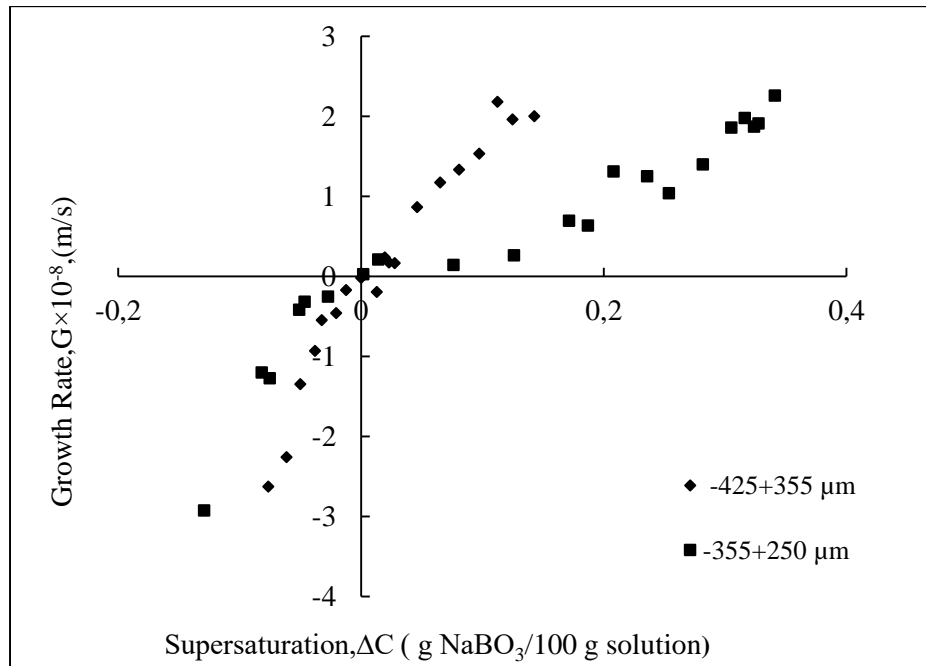


Figure 3.1. Growth and dissolution rate change for crystal size of $-425+355 \mu\text{m}$ and $-355+250 \mu\text{m}$ in stoichiometric media

Figure 3.1 shows that the dissolution rate of sodium perborate crystals does not show a significant change related to crystal size while the growth rate of sodium perborate crystals increases with increasing crystal size.

The change in the growth rate of sodium perborate crystals with respect to crystal size was determined by using Equation 3.1 for crystals with two different sizes ranges.

$$G = k \cdot \Delta C^g \quad (3.1)$$

The order of growth rate, g , is determined from the slope of the graph $\ln \Delta C$ versus $-\ln G$ and the growth rate constant, k , is determined from the intercept of the graph $\ln \Delta C$ versus $-\ln G$. The results are shown in Figure 3.2.

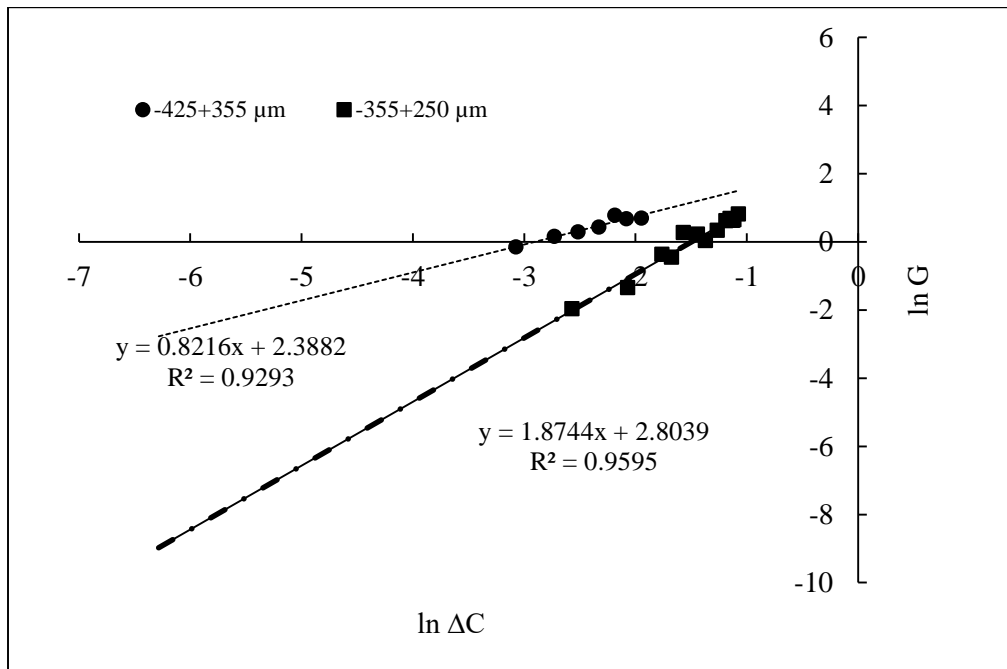


Figure 3.2. Determination of growth rate order of sodium perborate with crystal size of $-425+355 \mu\text{m}$ and $-355+250 \mu\text{m}$

As it is seen in Figure 3.2, the growth rate order was found 0.82 and 1.87 for crystals with size range of $-425+355 \mu\text{m}$ and $-355+250 \mu\text{m}$ respectively. This result shows that the crystal growth is diffusion controlled for larger crystal sizes and surface reaction controlled for smaller crystal sizes. The reason for the crystals with size range of $-425+355 \mu\text{m}$ having a higher growth rate than the crystals with size range of $-355+250 \mu\text{m}$ is that particles with larger crystal size requires high flow rate for fluidizing the particles which results diminishing the diffusion layer and fastens the growth rate. The crystals with crystal size range of $-355+250 \mu\text{m}$ is not affected by flow rate because of surface reaction controlled grow of the crystals. Due to the decrease in growth rate is

directly related to surface quality of crystals. Thus, as crystal size increase the surface defects of crystals decrease and grow regularly.

Microscopic photographs of sodium perborate tetrahydrate crystals used in the experiments and sodium perborate tetrahydrate crystals which were grown in pure media are shown in Figure 3.3 and 3.4 respectively.

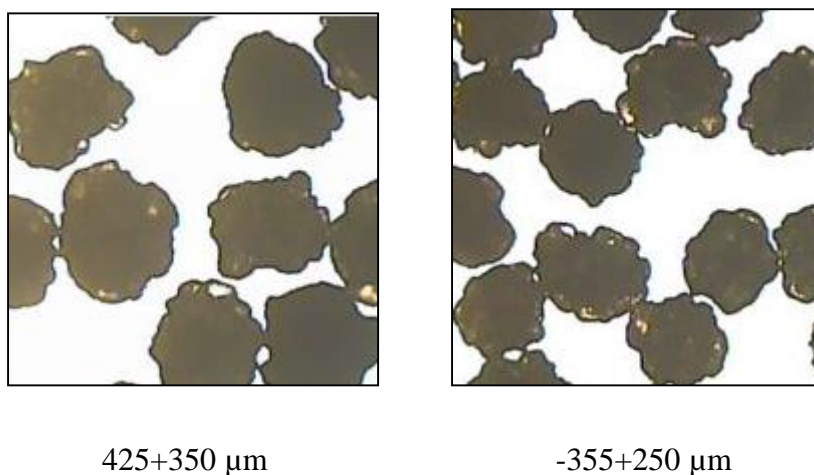


Figure 3.3. Microscopic photographs of sodium perborate tetrahydrate crystals used in experiments

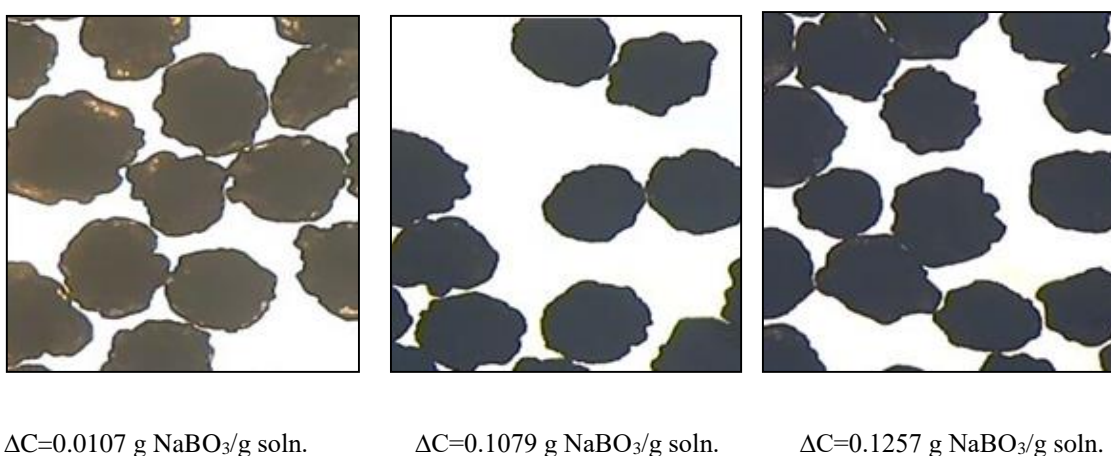


Figure 3.4. Microscopic photographs of sodium perborate tetrahydrate crystals grown in stoichiometric media

The crystals used in the experiments have cauliflower like appearance having spherical surface and do not consist of sharp surfaces. In the microscopic examination of the crystals which were grown in stoichiometric media, the crystals show similar cauliflower appearance and preserve the initial structure.

In order to investigate the effect of silica on the dissolution and growth rate of sodium perborate tetrahydrate crystals, the experiments were carried out with the silica concentration of 50, 250, 500, 1000 and 2000 ppm. The results for each silica concentration are shown in Appendix A between Figure A.1. and Figure A.5. The collective results are shown in Figure 3.5.

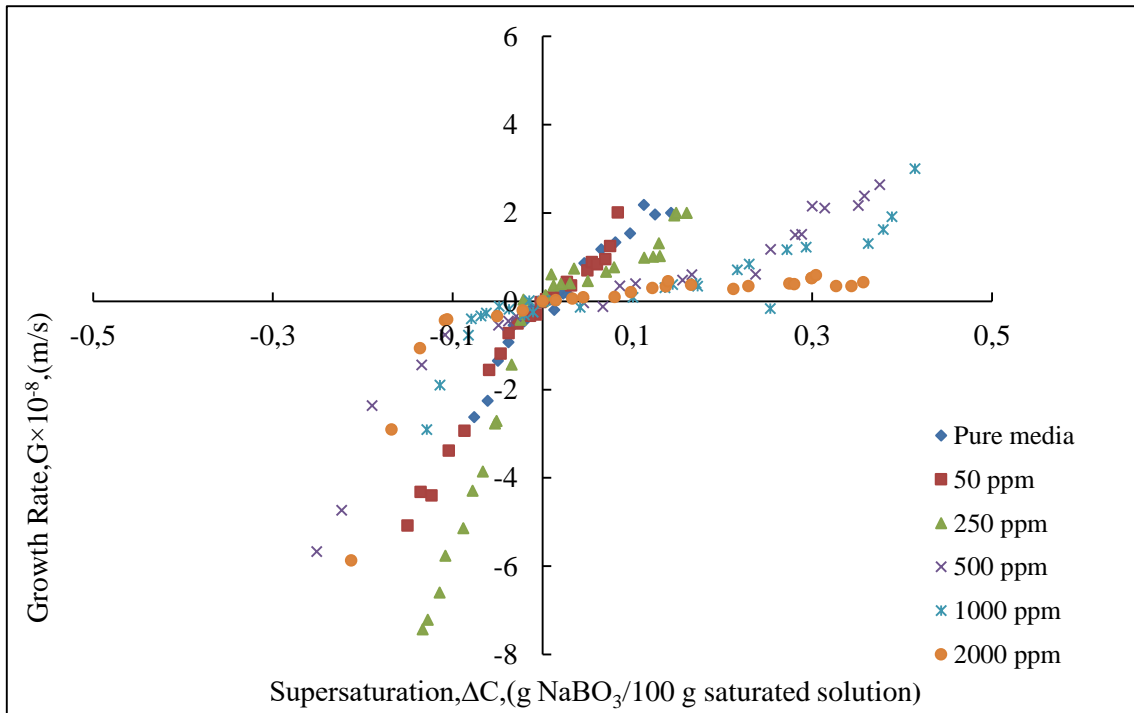


Figure 3.5. The effect of silica concentration on the growth and dissolution rates of sodium perborate tetrahydrate crystals in stoichiometric media

Figure 3.5 shows that the growth rate of sodium perborate tetrahydrate is suppressed as the silica concentration increases. In order to see the effect of silica obviously, the growth rates for three different supersaturation value were calculated and the change is shown in Figure 3.6.

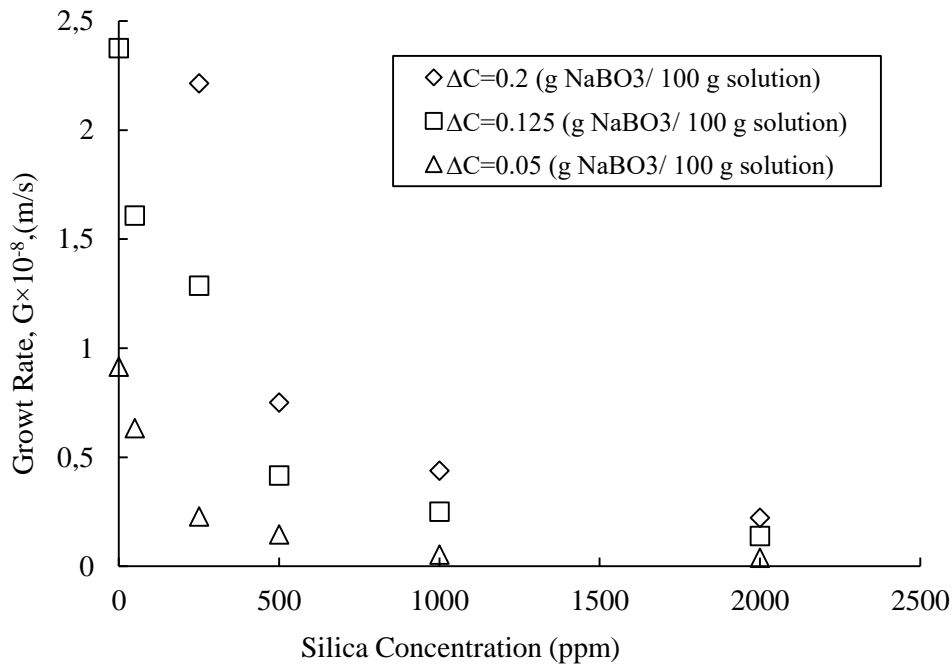


Figure 3.6. The change of the growth rate of sodium perborate tetrahydrate for selected supersaturation values in stoichiometric media

Figure 3.6 shows that as silica concentration increases the growth rate of sodium perborate is suppressed for selected supersaturation values. On the other hand, the growth rate shows the tendency of being suppressed effectively by silica concentration of 2000 ppm for each selected supersaturation values. According to this tendency obtained from the experiments, it can be said that the crystal growth can be blocked completely by higher silica concentration.

In order to determine the effect of silica on the growth rate order of sodium perborate tetrahydrate crystals in stoichiometric media, the evaluation made for pure media is also made for the results obtained from the presence of silica. The change of growth rate order depending on the silica concentration obtained as a result of the evaluation is shown in Figure 3.7 and the growth rate constant values are shown in Table 3.1.

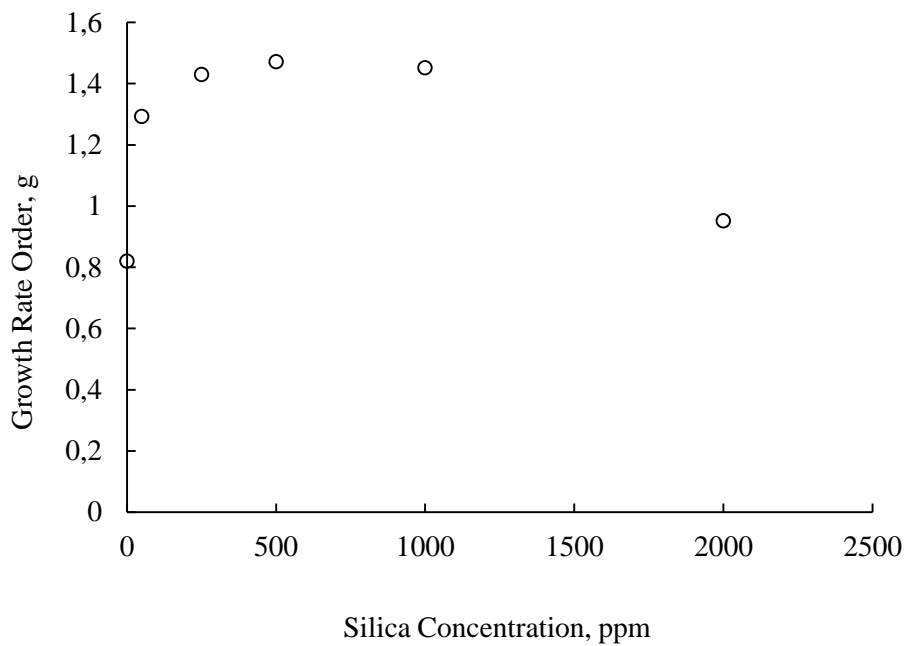


Figure 3.7. The effect of silica concentration on the growth rate order for stoichiometric media

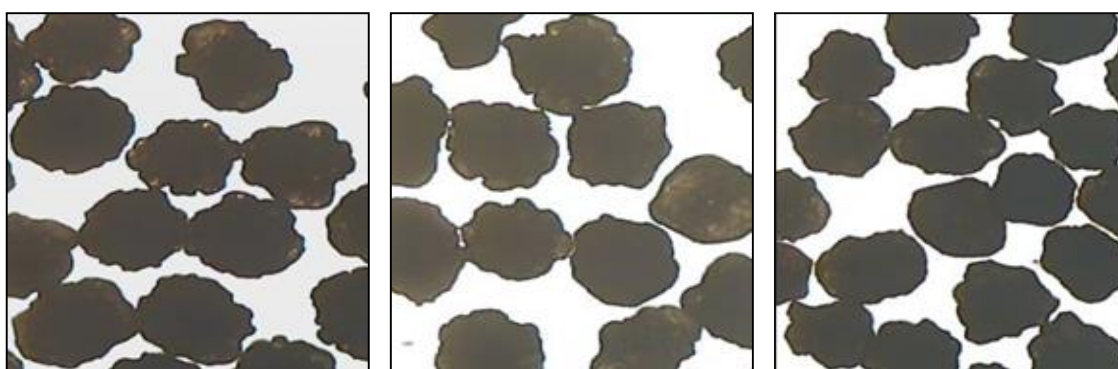
Table 3. 1 Growth rate constant values for stoichiometric media

| Silica Concentration (ppm) | 0 | 50 | 250 | 500 | 1000 | 2000 |
|----------------------------|--------|--------|-----|-------|-------|-------|
| Growth Rate Constant (m/s) | 10.894 | 34.953 | - | 9.659 | 6.292 | 1.474 |

Figure 3.7 shows that the growth rate order is affected by the silica concentration significantly. The growth rate order increases as the silica concentration increases until 1000 ppm and approaches to its value in stoichiometric media with the silica concentration of 2000 ppm. This indicates that diffusion controlled growth mechanism turns into surface reaction controlled mechanism with the increase in silica concentration. The decrease in the growth rate order at 2000 ppm of silica concentration

is caused by the extreme suppression of the growth rate rather than the change in growth rate mechanism.

The microscope photographs of sodium perborate tetrahydrate crystals grown in stoichiometric media in the presence of silica in stoichiometric media are shown between Figure 3.8 and Figure 3.12.



$\Delta C = 0.0116$ g NaBO₃/g soln.

$\Delta C = 0.0498$ g NaBO₃/g soln.

$\Delta C = 0.0838$ g NaBO₃/g soln.

Figure 3.8. The microscope photographs of sodium perborate tetrahydrate crystals in stoichiometric media for 50 ppm silica concentration

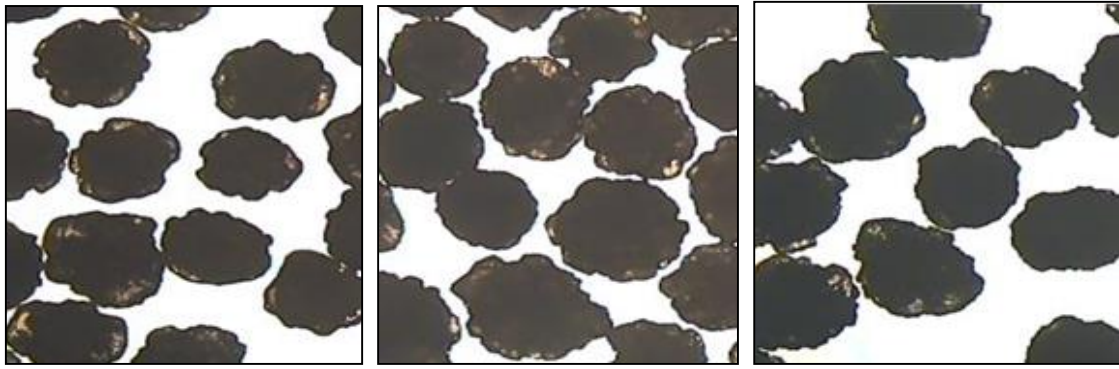


$\Delta C = 0.0120$ g NaBO₃/g soln.

$\Delta C = 0.0618$ g NaBO₃/g soln.

$\Delta C = 0.0811$ g NaBO₃/g soln.

Figure 3.9. The microscope photographs of sodium perborate tetrahydrate crystals in stoichiometric media for 250 ppm silica concentration



$\Delta C=0.0259$ g NaBO₃/g soln.

$\Delta C=0.1595$ g NaBO₃/g soln.

$\Delta C=0.2106$ g NaBO₃/g soln.

Figure 3.10. The microscope photographs of sodium perborate tetrahydrate crystals in stochiometric media for 500 ppm silica concentration

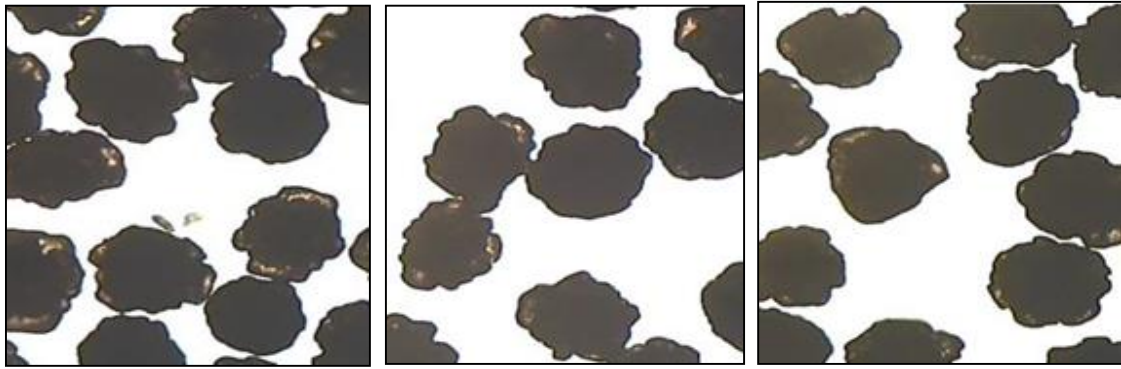


$\Delta C=0.0255$ g NaBO₃/g soln.

$\Delta C=0.1193$ g NaBO₃/g soln.

$\Delta C=0.2518$ g NaBO₃ /g soln.

Figure 3.11. The microscope photographs of sodium perborate tetrahydrate crystals in stochiometric media for 1000 ppm silica concentration



$\Delta C=0.0261$ g NaBO_3 /g soln.

$\Delta C=0.1014$ g NaBO_3 /g soln.

$\Delta C=0.2156$ g NaBO_3 /g soln.

Figure 3.12. The microscope photographs of sodium perborate tetrahydrate crystals in stochiometric media for 2000 ppm silica concentration

It is seen that; crystals grown in the presence of silica have the cauliflower like appearance as well and sharp edged surfaces appear. This effect is increased as silica concentration increased. As a result of this, crystal appearance has become different.

The solubility change of sodium perborate tetrahydrate in water and in the presence of different free sodium metaborate values is given in Figure 3.13

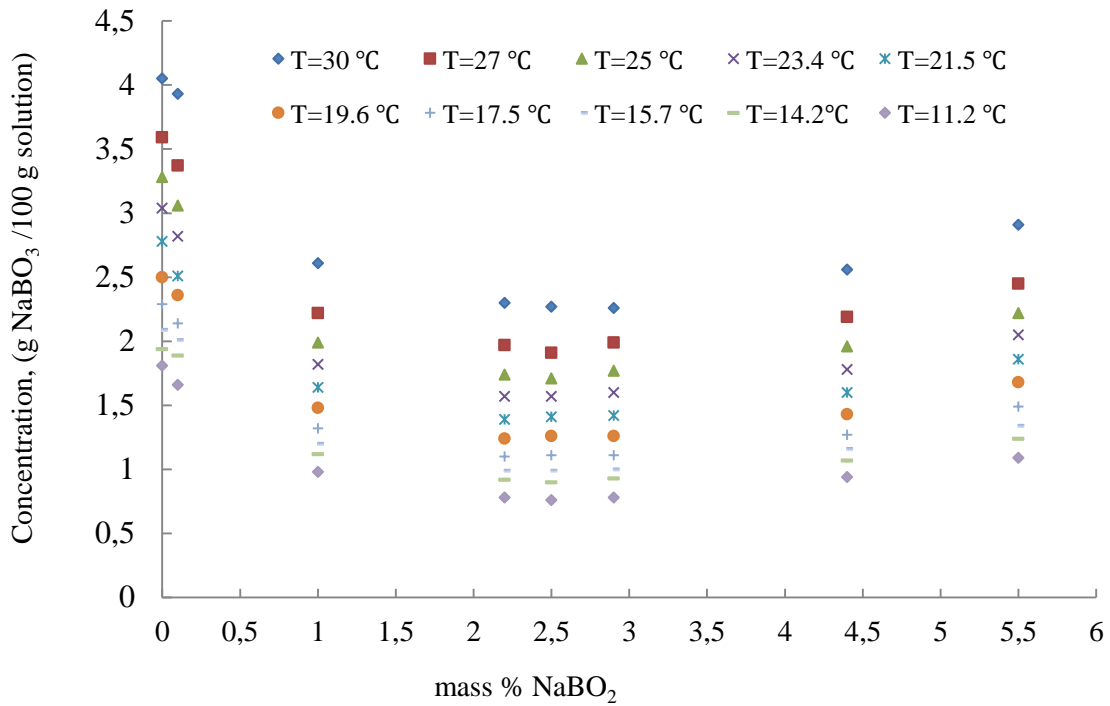


Figure 3.13. Dependence of solubility of sodium perborate tetrahydrate on NaBO₂ concentration

Figure 3.13 shows that the solubility of sodium perborate decreases until 2% metaborate concentration by weight, remains constant between 2-3% metaborate concentration by weight and after increases. Considering that the metaborate concentration remains constant between 2 % and 3 %, the growth rate of sodium perborate tetrahydrate crystals were determined in the presence of 2.5 % metaborate concentration. As the results were evaluating, the change in the concentration of sodium perborate was taken into account and the supersaturation values were obtained from the solubility graph in Figure 3.13. In the presence of 2.5% (w/w) NaBO₂, the dissolution and growth rate of sodium perborate for pure media and in the presence of silica 50, 250, 500, 1000 and 2000 ppm are shown in Appendix B. The collective results are shown in Figure 3.14.

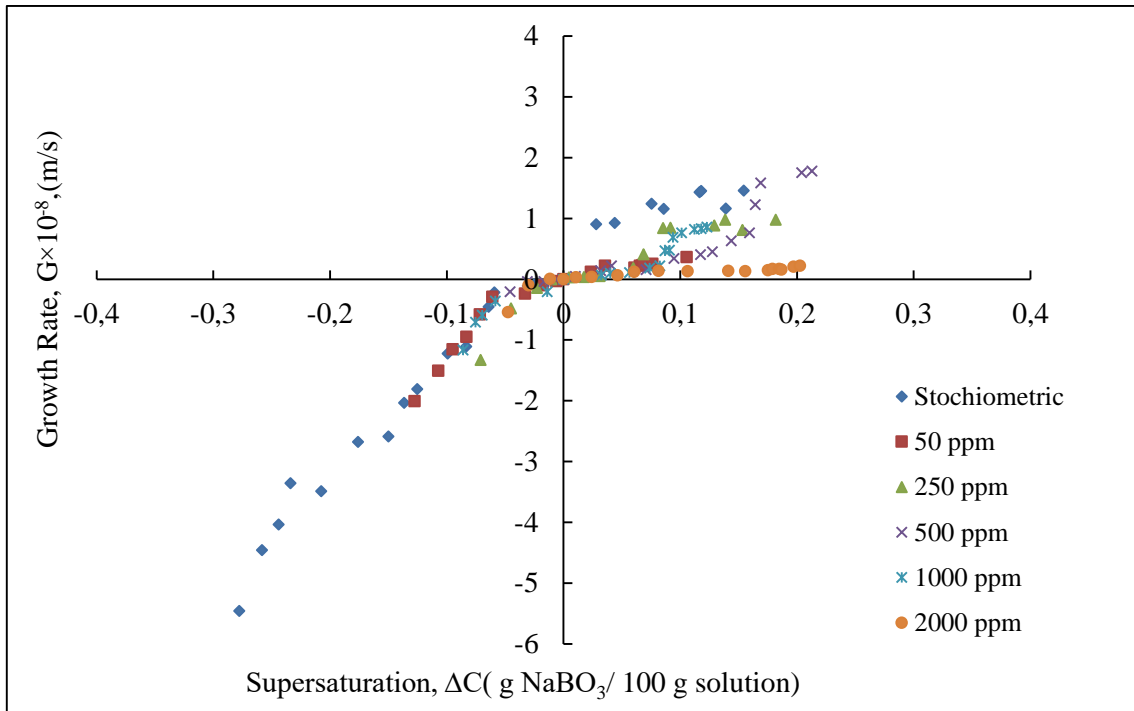


Figure 3.14. The effect of silica on growth and dissolution rates of sodium perborate tetrahydrate in the presence of 2.5 % (w/w) NaBO_2

As it can be seen in Figure 3.13, the growth rate of sodium perborate tetrahydrate is suppressed in the presence of 2.5 % (w/w) NaBO_2 . Similar to the evaluation that was made for the stochiometric media, in order to see the silica effect clearly, the growth rates for three selected supersaturation values were calculated. The results are shown in Figure 3.15.

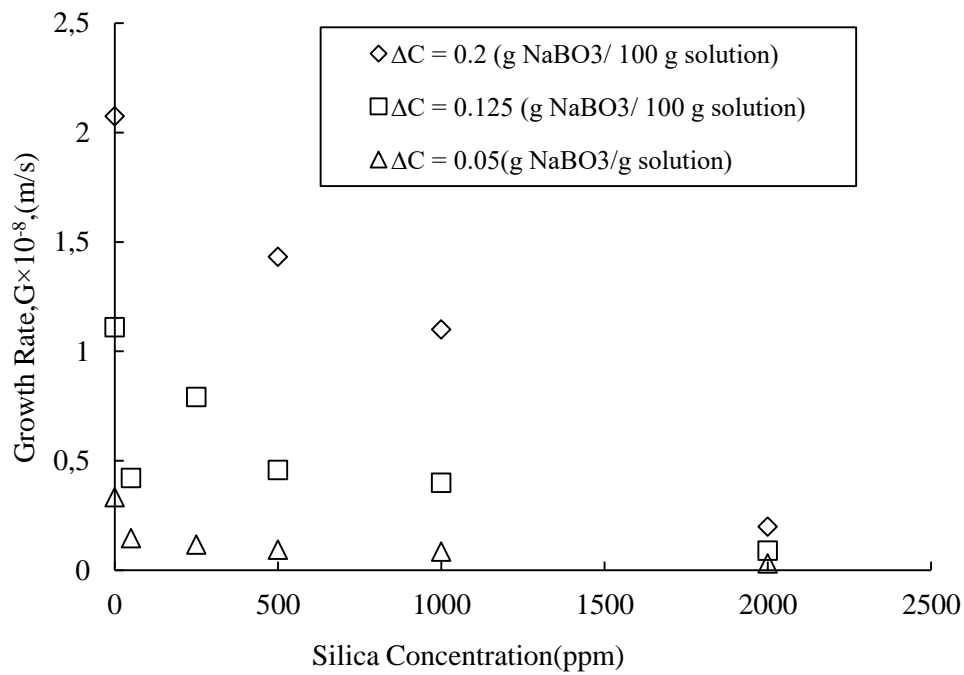


Figure 3.15. The change of the growth rate of sodium perborate tetrahydrate crystals for selected supersaturation values in the presence of 2.5 % (w/w) NaBO₂

It can be seen in Figure 3.15 that the growth rate of sodium perborate tetrahydrate crystals is suppressed as the silica concentration increases for the selected supersaturation values in the presence of 2,5% (w/w) NaBO₂ similar to the results obtained for stoichiometric media. In order to see the effect of silica with respect to the conditions of the media, the growth rate values for two selected supersaturation values were given in Figure 3.16 and Figure 3.17.

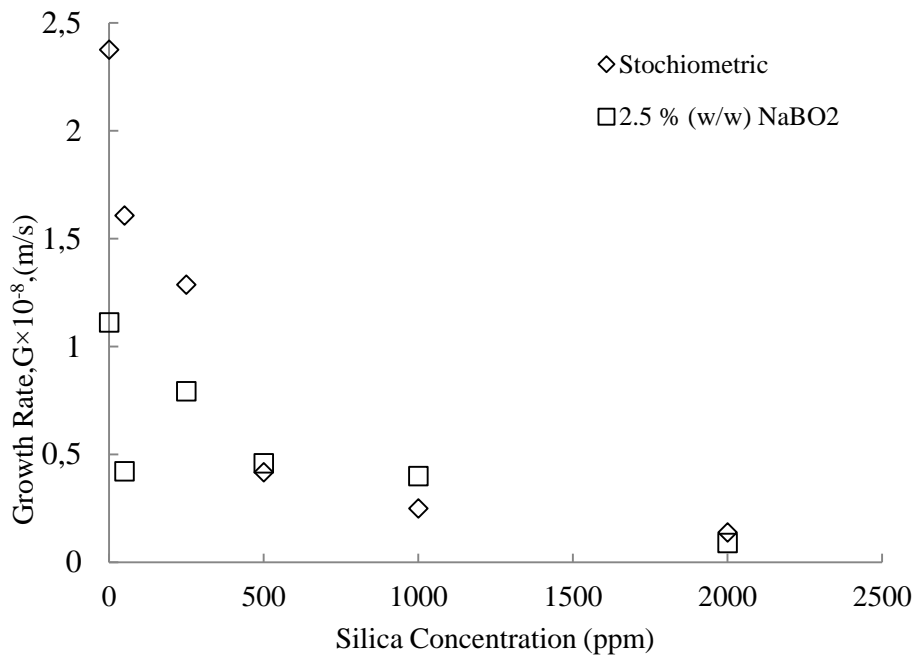


Figure 3.16. Growth rate change for stoichiometric media and in the presence of 2.5% (w/w) NaBO₂ for $\Delta C=0.125$ g NaBO₃ /100 g solution

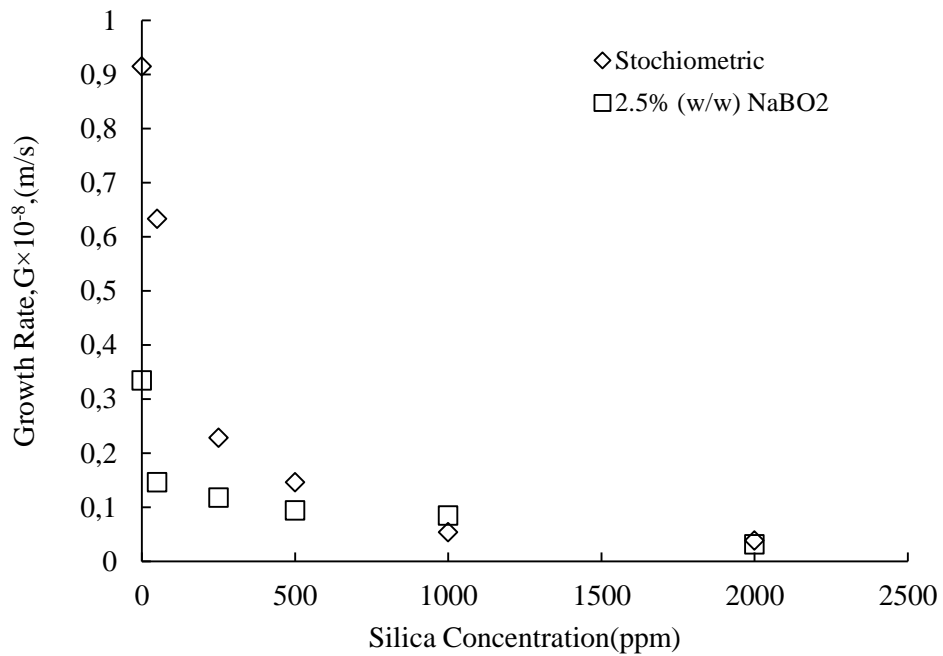


Figure 3.17. Growth rate change for stoichiometric media and in the presence of 2.5% (w/w) NaBO₂ for $\Delta C=0.05$ g NaBO₃ /100 g solution

Figure 3.16 and 3.17 demonstrate that the growth rate of sodium perborate is suppressed significantly in the presence of 2.5 % (w/w) NaBO₂ in pure media. While at low silica concentrations, in the presence of NaBO₂ the suppression of the growth rate is more effective, at 500 ppm or higher silica concentrations the growth rate is controlled by the presence of silica. This effect is observed in each supersaturation values.

The effect of silica on the growth rate order of sodium perborate crystals in the presence of 2.5 % (w/w) NaBO₂ is shown in Figure 3.18 and the growth rate constants are shown in Table 3.2.

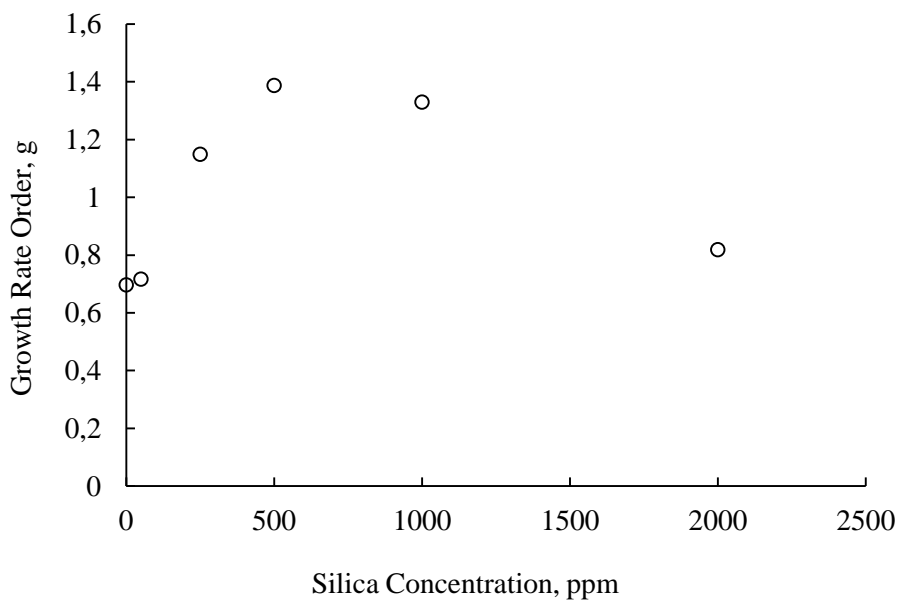


Figure 3.18. The effect of silica concentration on the growth rate order in the presence of 2.5 % (w/w) NaBO₂

Table 3. 2 Growth rate constant values for 2.5 % (w/w) NaBO₂

| Silica Concentration (ppm) | 0 | 50 | 250 | 500 | 1000 | 2000 |
|----------------------------|-------|-------|-------|--------|--------|-------|
| Growth Rate Constant (m/s) | 5.696 | 1.644 | 6.638 | 12.001 | 48.216 | 0.865 |

As it can be seen in Figure 3.18 that the growth rate order of sodium perborate tetrahydrate is affected much by the presence of silica. The growth rate order increases until silica concentration of 500 ppm and then it shows the tendency of decreasing. This tendency shows similarity to the results that were obtained for stoichiometric media. In order to see the effect of sodium metaborate excess on the growth rate order, the growth rate order versus silica concentration graph is plotted and shown in Figure 3.19.

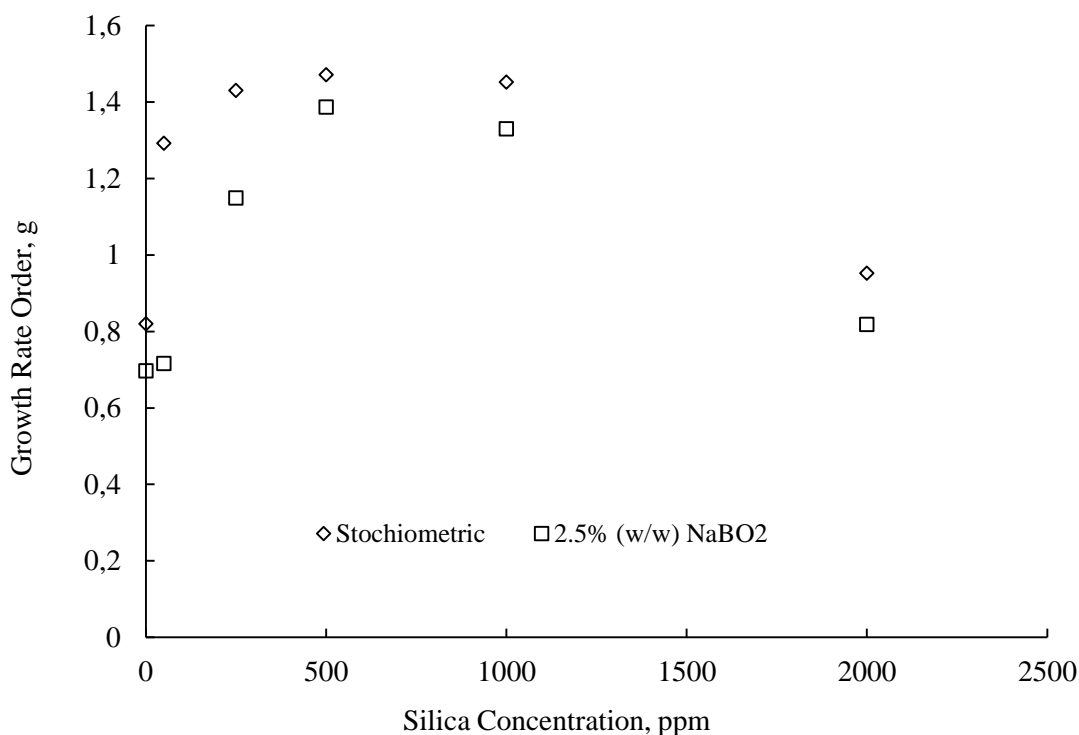
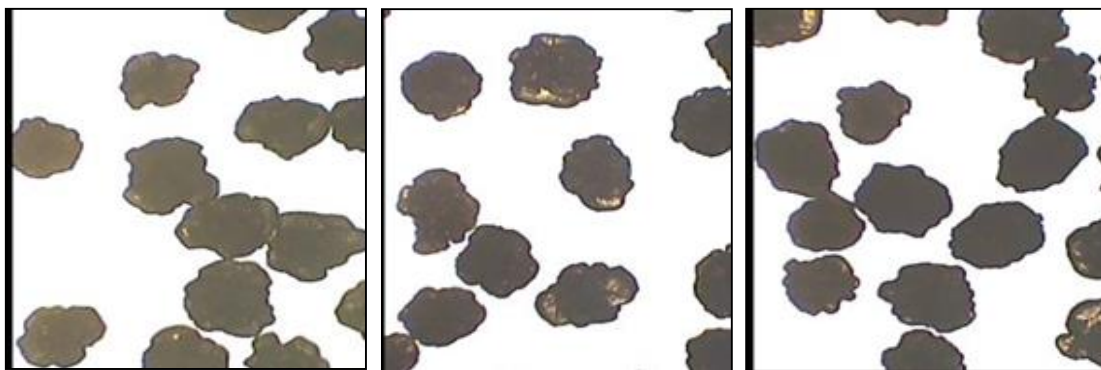


Figure 3.19. The change of the growth rate order for stoichiometric media and in the presence of 2.5% (w/w) NaBO₂

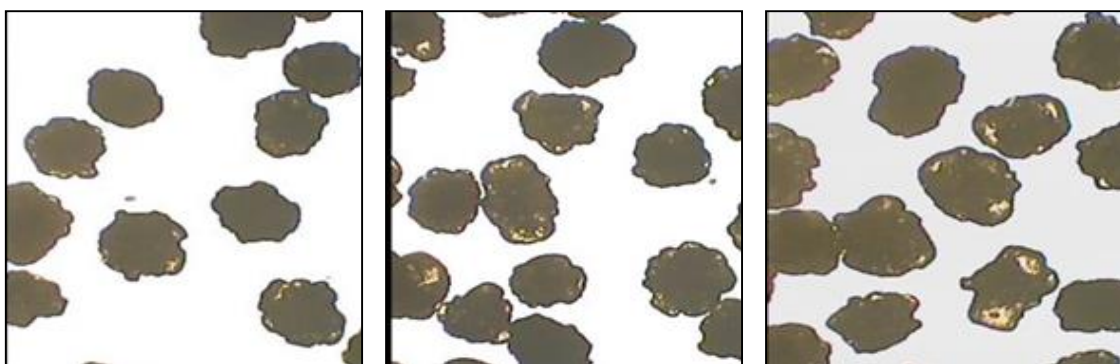
As it is seen clearly in Figure 19; that sodium metaborate excess causes decrease in growth rate order in pure media and with all silica concentrations compared to stoichiometric media.

The microscopic photographs of sodium perborate tetrahydrate crystals grown in the presence of 2.5 % (w/w) NaBO₂ for different silica concentrations are shown between Figure 3.20 and 3.25.



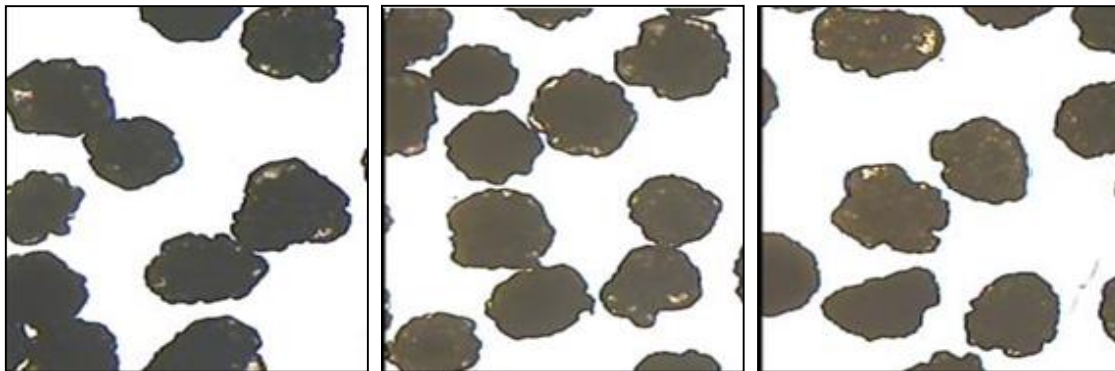
$\Delta C=0.0209$ g NaBO₃/100 g soln. $\Delta C=0.1089$ g NaBO₃/100 g soln. $\Delta C=0.1723$ g NaBO₃/100 g soln.

Figure 3.20. Microscopic photographs of sodium perborate tetrahydrate crystals grown in the presence of 2.5 % (w/w) NaBO₂ in pure media



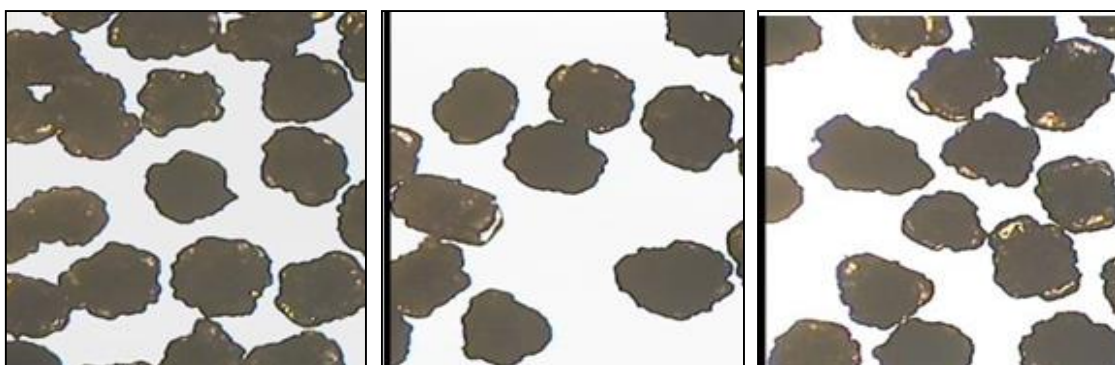
$\Delta C=0.0102$ g NaBO₃/100 g soln. $\Delta C= 0.0522$ g NaBO₃/100 g soln. $\Delta C= 0.0922$ g NaBO₃/100 g soln.

Figure 3.21. Microscopic photographs of sodium perborate tetrahydrate crystals grown in the presence of 2.5 % (w/w) NaBO₂ for 50 ppm silica concentration



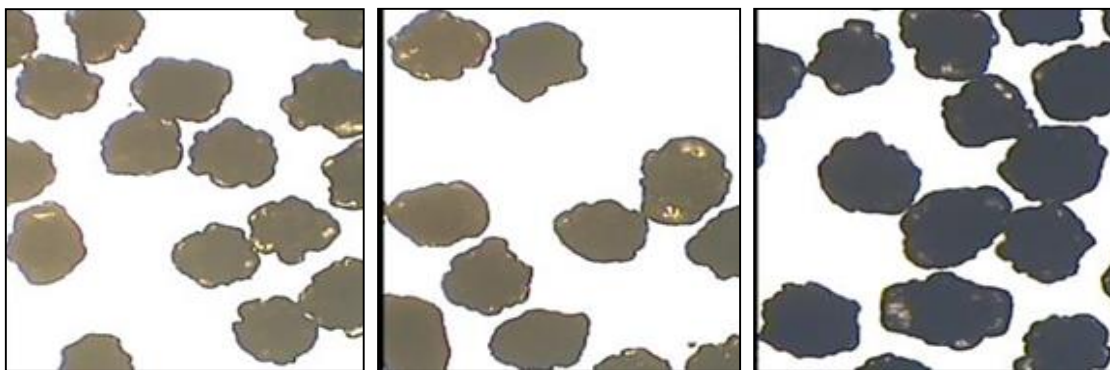
$\Delta C=0.0173$ g NaBO₃/100 g soln. $\Delta C=0.1289$ g NaBO₃/100 g soln. $\Delta C=0.1816$ g NaBO₃/100 g soln.

Figure 3.22. Microscopic photographs of sodium perborate tetrahydrate crystals grown in the presence of 2.5% (w/w) NaBO₂ for 250 ppm silica concentration



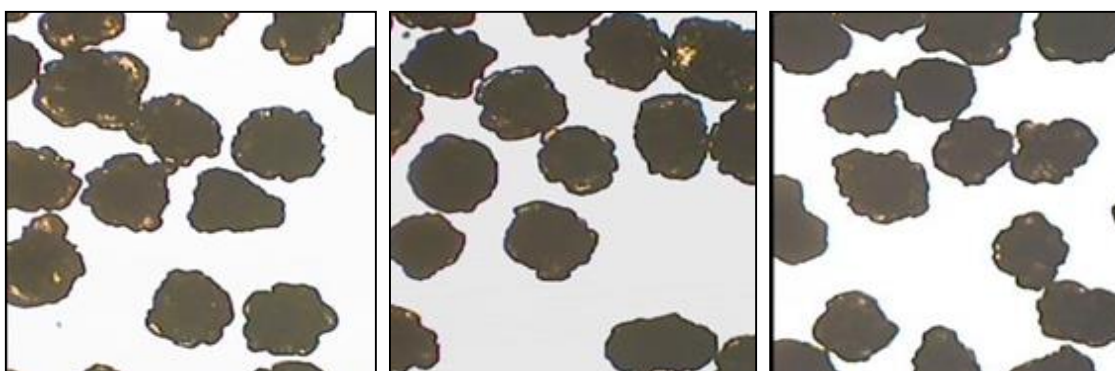
$\Delta C= 0.0101$ g NaBO₃/100 g soln. $\Delta C=0.1273$ g NaBO₃/100 g soln. $\Delta C=0.1688$ g NaBO₃/100 g soln.

Figure 3.23 Microscopic photographs of sodium perborate tetrahydrate crystals grown in the presence of 2.5% (w/w) NaBO₂ for 500 ppm silica concentration



$\Delta C = 0.0121$ g $\text{NaBO}_3/100$ g soln. $\Delta C = 0.0415$ g $\text{NaBO}_3/100$ g soln. $\Delta C = 0.0523$ g $\text{NaBO}_3/100$ g soln.

Figure 3.24. Microscopic photographs of sodium perborate tetrahydrate crystals grown in the presence of 2.5% (w/w) NaBO_2 for 1000 ppm silica concentration



$\Delta C = 0.0279$ g $\text{NaBO}_3/100$ g soln. $\Delta C = 0.1024$ g $\text{NaBO}_3/100$ g soln. $\Delta C = 0.1491$ g $\text{NaBO}_3/100$ g soln.

Figure 3.25. Microscopic photographs of sodium perborate tetrahydrate crystals grown in the presence of 2.5% (w/w) NaBO_2 for 2000 ppm silica concentration

The microscopic photographs of crystals grown in the presence of 2.5% (w/w) NaBO_2 showed that the cauliflower like appearance of sodium perborate tetrahydrate crystals has diminished compared to the crystals grown in stoichiometric media. Also it is observed that the sharp edged surfaces, which grow from the main body, have increased. Presence of silica in medium did not change this result. Thus, it can be said that this type of

growth was caused by the presence of sodium metaborate rather than the presence of silica. Considering that; the presence of sodium metaborate and silica suppressed the growth rate of sodium perborate tetrahydrate, it is clear that the growth will be slower but more properly which will result to have a compact crystal appearance. Thus, the results obtained from the experiments support this thought.

4. CONCLUSIONS

The following results have been obtained in this study which the growth and dissolution rates of sodium perborate tetrahydrate were measured in stoichiometric media and with 2.5% (w/w) NaBO₂.

1. The dissolution rate of sodium perborate tetrahydrate crystals are not affected by the crystal size while the growth rate increases as the crystal size increases.
2. It is obtained that the growth rate of sodium perborate crystals with a crystal size range of -425+355 μm is diffusion controlled and the growth rate of sodium perborate crystals with crystal size range of -355+250 μm is surface reaction controlled.
3. The growth rate of sodium perborate tetrahydrate is suppressed depending on the silica concentration. It is observed that at high silica concentration the growth can be stopped completely.
4. The growth rate order is affected reasonably by the silica concentration in stoichiometric media. The diffusion controlled mechanism in stoichiometric media turns into surface reaction controlled as the silica concentration increases.
5. The growth rate of sodium perborate tetrahydrate crystals is suppressed with 2.5 % (w/w) NaBO₂.
6. The effect of silica on the growth rate of sodium perborate tetrahydrate is more effective at high silica concentrations with 2.5 % (w/w) NaBO₂.
7. The diffusion controlled growth rate mechanism with 2.5% (w/w) NaBO₂, which is similar to stoichiometric media, turns into surface controlled mechanism as the silica concentration increases. Also, the growth rate order with 2.5 % (w/w) decreases for each silica concentration compared to stoichiometric media.
8. The appearance of sodium perborate crystals has changed due to silica concentration and the presence of 2.5% (w/w) NaBO₂.

The structure of sodium perborate tetrahydrate crystals have sharper surfaces in the presence of silica in stoichiometric media and in the presence of 2.5% (w/w) NaBO_2 excess. This clearly shows that the mechanical strength of crystals will increase. The presence of silica in the presence of 2.5% (w/w) NaBO_2 has not changed this effect caused from sodium metaborate on the crystal appearance. Considering all results obtained in the experiments, it can be concluded that the production of sodium perborate tetrahydrate can take place in the presence of 2.5% (w/w) NaBO_2 and using silica as stabilizer do not create a negative impact.

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APPENDIX A

THE GROWTH AND DISSOLUTION RATES OF SODIUM PERBORATE TETRAHYDRATE CRYSTALS IN STOICHIOMETRIC MEDIA

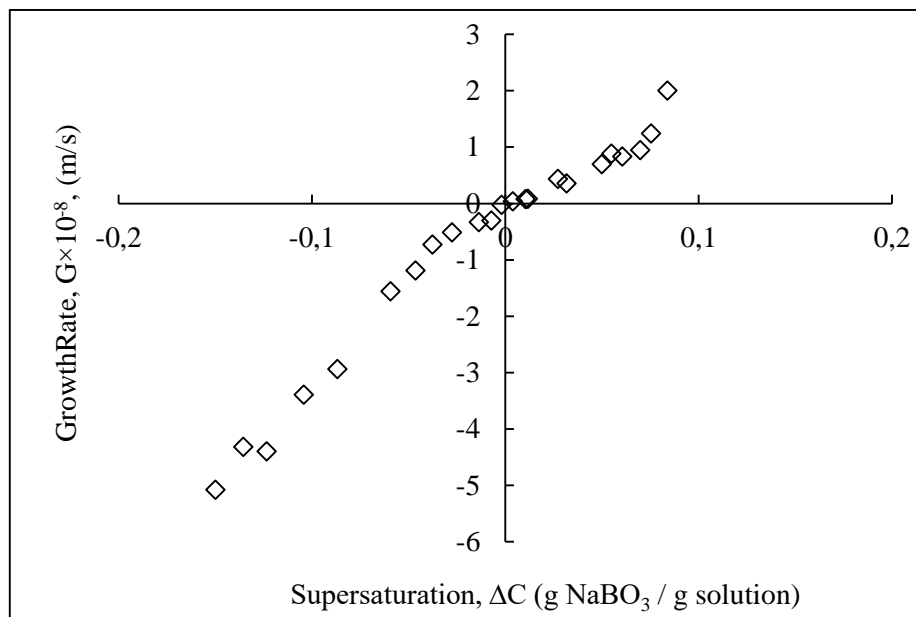


Figure A.1. The dissolution and growth rates of sodium perborate tetrahydrate crystals for 50 ppm silica concentration

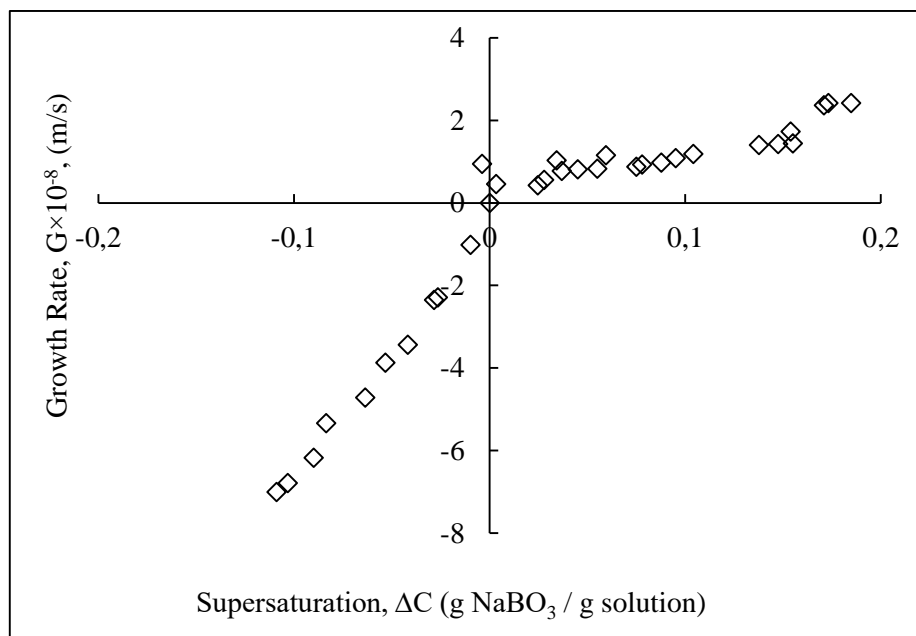


Figure A.2. The dissolution and growth rates of sodium perborate tetrahydrate crystals for 250 ppm silica concentration

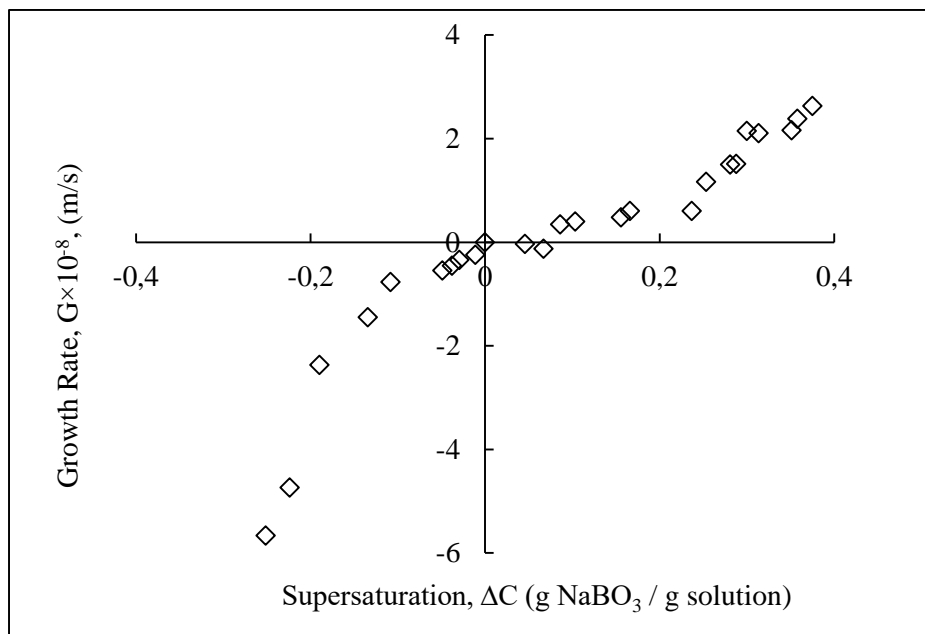


Figure A.3. The dissolution and growth rates of sodium perborate tetrahydrate crystals for 500 ppm silica concentration

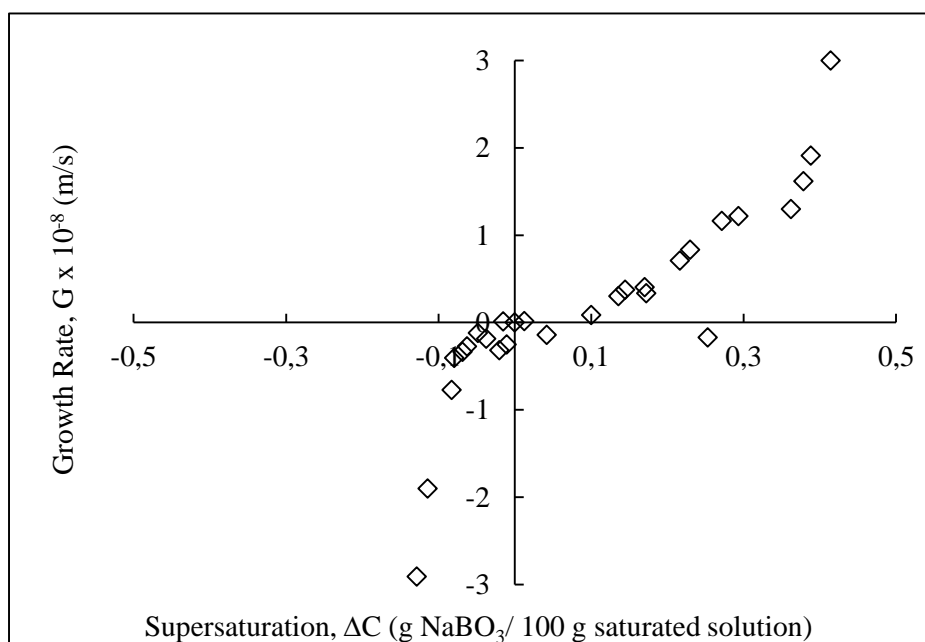


Figure A.4. The dissolution and growth rates of sodium perborate tetrahydrate crystals for 1000 ppm silica concentration

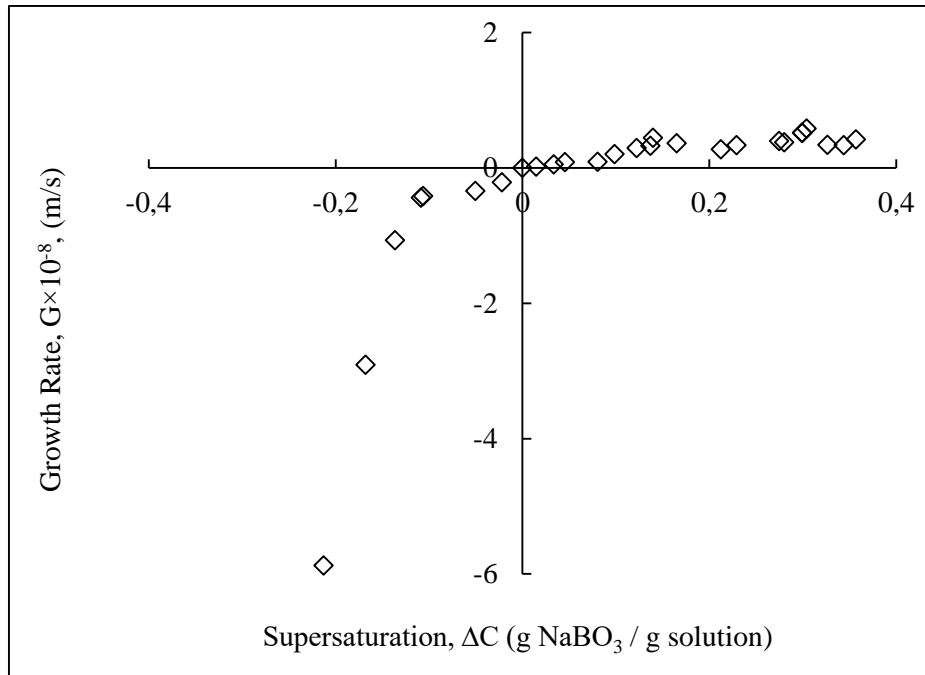


Figure A.5. The dissolution and growth rates of sodium perborate tetrahydrate crystals for 2000 ppm silica concentration

APPENDIX B

THE GROWTH AND DISSOLUTION RATES OF SODIUM PERBORATE TETRAHYDRATE CRYSTALS IN THE PRESENCE OF 2.5 % (w/w) NaBO₂

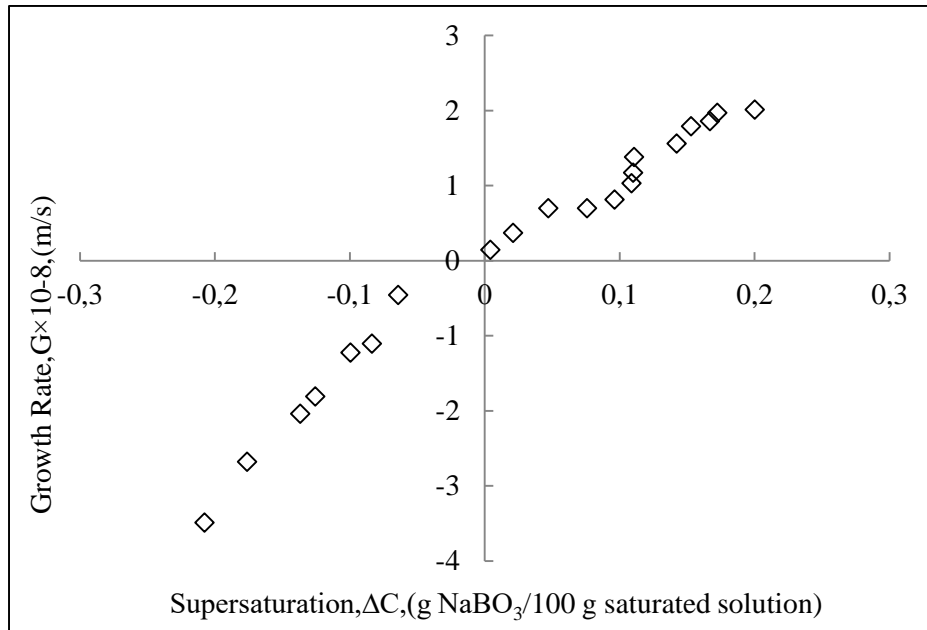


Figure B.1. The dissolution and growth rates of sodium perborate tetrahydrate crystals in the presence of 2.5 % (w/w) NaBO₂ for pure media

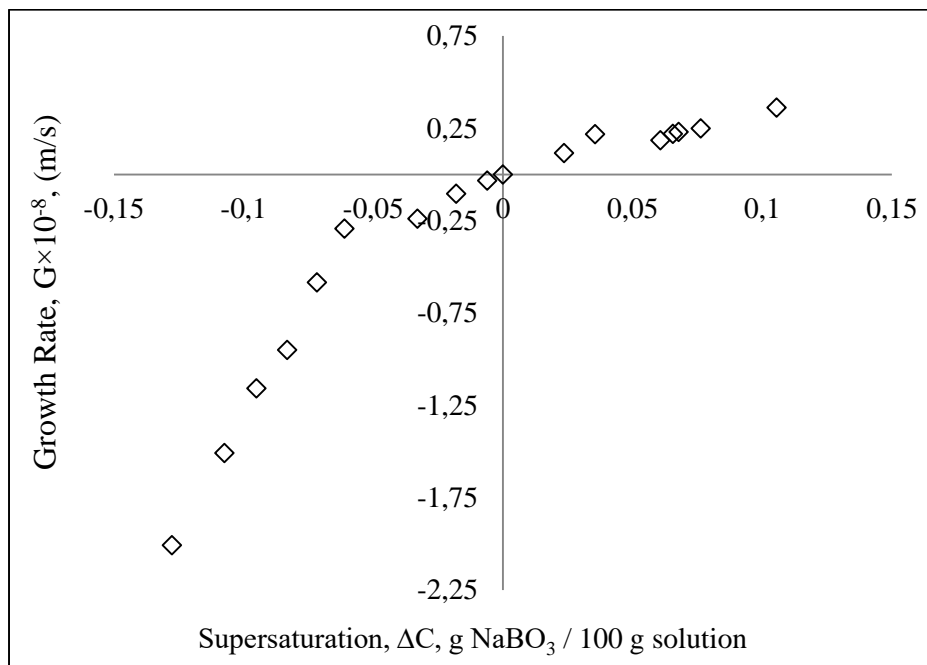


Figure B.2. The dissolution and growth rates of sodium perborate tetrahydrate crystals in the presence of 2.5 % (w/w) NaBO₂ for 50 ppm silica concentration

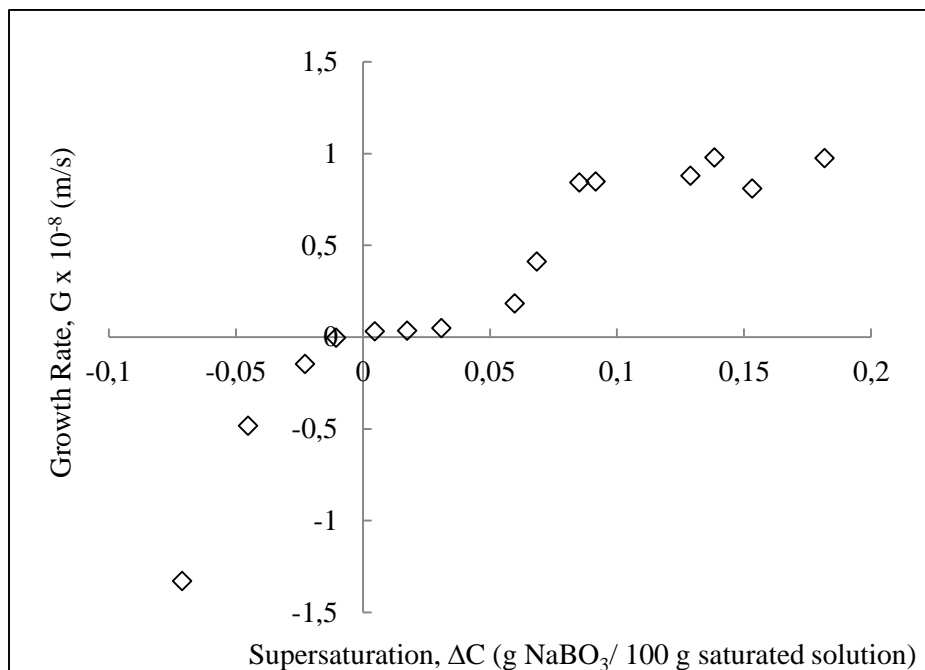


Figure B.3. The dissolution and growth rates of sodium perborate tetrahydrate crystals in the presence of 2.5 % (w/w) NaBO₂ for 250 ppm silica concentration

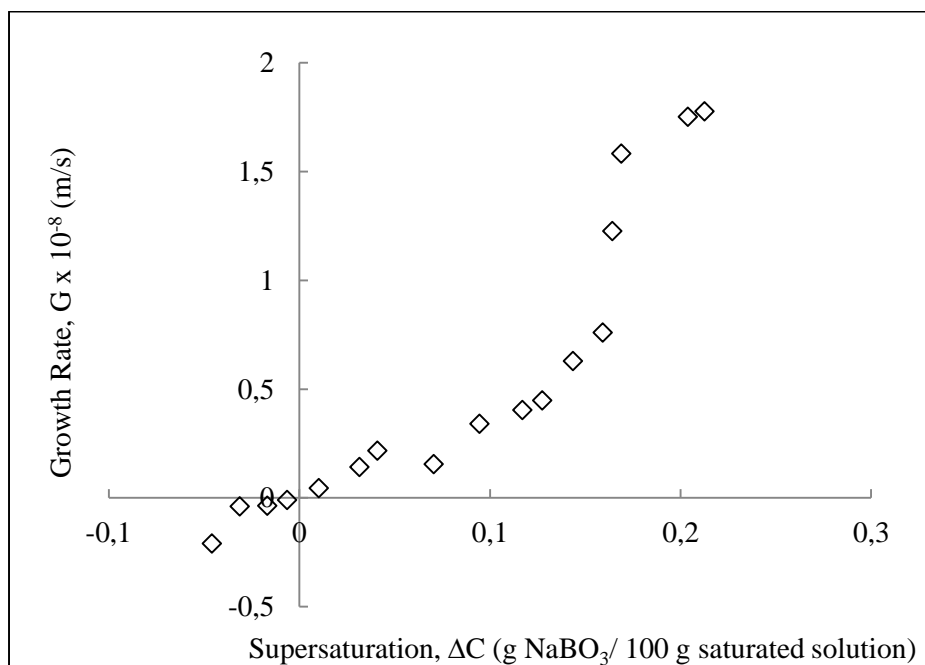


Figure B.4. The dissolution and growth rates of sodium perborate tetrahydrate crystals in the presence of 2.5 % (w/w) NaBO₂ for 500 ppm of silica concentration

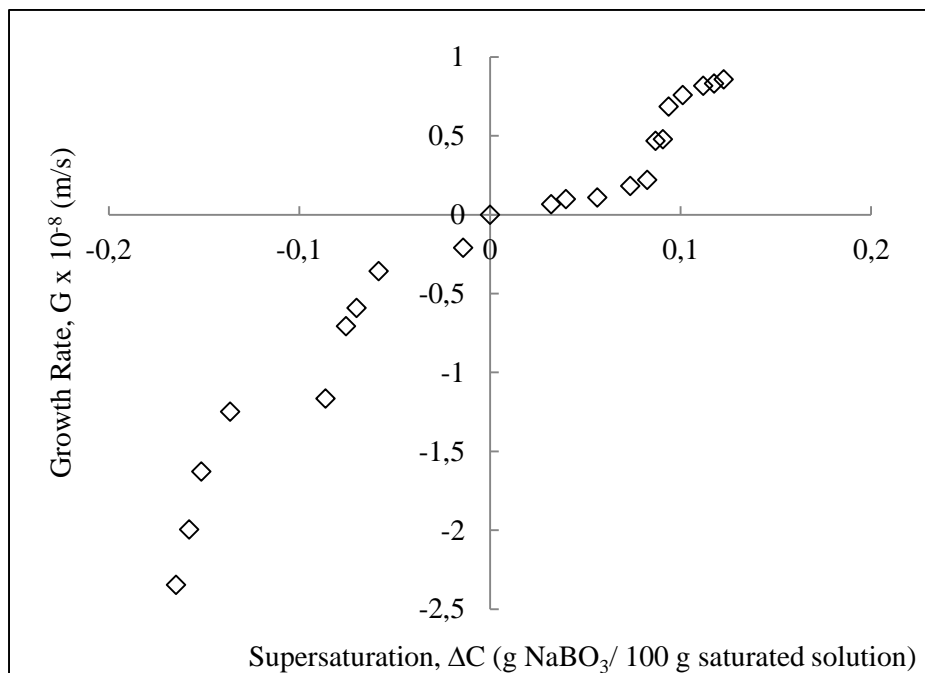


Figure B.5. The dissolution and growth rates of sodium perborate tetrahydrate crystals in the presence of 2.5 % (w/w) NaBO₂ for 1000 ppm of silica concentration

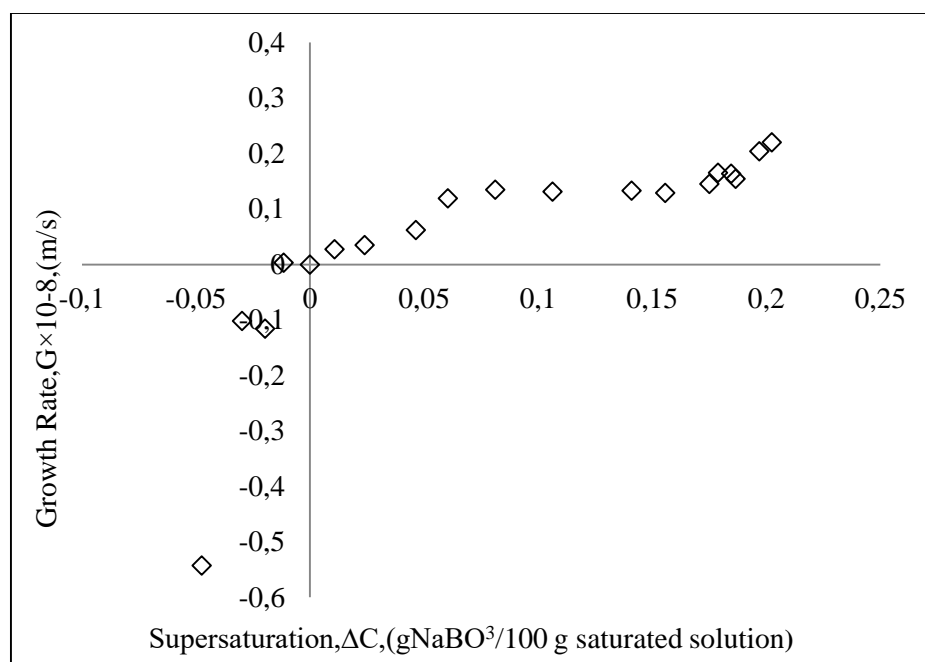


Figure B.6. The dissolution and growth rates of sodium perborate tetrahydrate crystals in the presence of 2.5 % (w/w) NaBO₂ for 2000 ppm of silica concentration

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