SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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MORPHOLOGICAL INVESTIGATION OF PRECIPITATED CALCIUM CARBONATE (PCC) CHARACTERISTICS WITH THE PRESENCE OF ADDITIVES DURING SYNTHESIS

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Morphological Investigation of Precipitated Calcium Carbonate (PCC) Characteristics with the Presence of Additives during Synthesis**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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LIST OF ABBREVIATION

EDTA	Ethylediaminetetraacetic acid
FTIR	Fourier Transform Infrared Spectroscopy
LOI	Loss on Ignition
PVA	Poly-vinyl alcohol
M	Molar
MOL	Milk of Lime
PCC	Precipitated Calcium Carbonate
PSA	Particle Size Analysis
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

LIST OF SYMBOLS

°C	Degree celcius
%	Percentage
CO_2	Carbon dioxide
CaO	Calcium oxide
$Ca(OH)_2$	Calcium hydroxide
wt%	weight percentage
$CaCO_3$	calcium carbonate
H_2O	water
L	liter
G	gram
D_{10}	10% volume of the particles have a size value lower than or equal to D_{10}
D_{50}	50% volume of the particles have a size value lower than or equal to D_{50}
D_{90}	90% volume of the particles have a size value lower than or equal to D_{90}

UNTUK MENGKAJI KRISTAL MORFOLOGI BAGI CIRI-CIRI KALSIUM KARBONAT (PCC) DALAM PENAMBAHAN ADIKTIF SEMASA SINTESIS

ABSTRAK

Kajian ini dijalankan untuk menyiasat morfologi kristal pada kalsium karbonat (PCC) semasa sintesis proses dengan kehadiran aditif. Parameter mengawal seperti kepekatan kalsium hidroksida ("milk of lime") dan kadar aliran gas karbon dioksida mem pengaruhi saiz zarah dan polimorf kristal kalsium karbonat. Dalam kajian ini, dua jenis adiktif telah digunakan untuk perbandingan berdasarkan ciri-ciri kalsium karbonat dicetuskan. Adiktif mengubah permukaan bahan kristal dan saiz zarah. Ia mendapati bahawa kalsium karbonat dengan penambahan EDTA, EDTA menukar kristal calcite rombohedral ke kalsit sfera atau kalsit prisma. PCC banyak digunakan dalam banyak aplikasi kerana kestabilan PCC berbanding bahan lain, keputihan tulen PCC dan keserasian PCC bercampur dengan bahan lain. Kadar aliran gas karbon dioksida yang bertambah ke dalam larutan kalsium hidroksida mnemambahkan saiz partikel kirstal PCC. 20ml / min dan 10ml / min telah dipilih untuk mengkaji kesan terhadap polimorf. Peningkatan kepekatan "milk of lime" akan memberi kesan kepada bentuk kirstal PCC. 0.9M dan 0.5M kepekatan yang digunakan dalam kajian ini untuk mengkaji bagaimana kepekatan "milk of lime"memainkan peranan dalam mempengaruhi polimorf PCC. Oleh itu, semua parameter yang dikawal perlu dipertimbangkan sebelum memulakan sintesis kalsium karbonat.

MORPHOLOGICAL INVESTIGATION OF PRECIPITATED CALCIUM CARBONATE (PCC) CHARACTERISTICS IN THE PRESENCE OF ADDITIVES DURING SYNTHESIS

ABSTRACT

The research was conducted in order to investigate the crystal morphology of precipitated calcium carbonate (PCC) characteristics during the synthesis with the presence of additives. The controlling variables such as concentration of calcium hydroxide (milk of lime) and flow rate of carbon dioxide gas influences the particle size and polymorph of crystal of precipitated calcium carbonate. In this research, two types of additives are being used to distinguish based on the precipitated calcium carbonate characteristics. An additive changes the surface of crystal materials and particle size. It was found that slaked lime in the presence of EDTA changing the rhombohedral calcite crystal into spherical calcite or prismatic calcite. PCC widely being used in many applications because of the stability of PCC compare others, the pure whiteness of PCC and the compatibility of PCC mixed with others. Increases flow rate of carbon dioxide gas into the calcium hydroxide solution affected the size particle of suspension of PCC. 20ml/min and 10ml/min were being chosen to study the effect of rate flow of carbon dioxide gas towards the polymorph. The increases concentration of "milk of lime" will change the shape crystal suspension of PCC. 0.9M and 0.5M concentration of calcium hydroxide being used in this research to study how concentration of "milk of lime" plays a role in influences of polymorph of PCC. Thus, all the parameters need to consider before begins synthesis of calcium carbonate.

CHAPTER 1

INTRODUCTION

1.1 Background of PCC

Precipitated calcium carbonate (PCC) is an innovative product through the synthesizing process of calcium carbonate where it can be used in many of applications (www.lime.org). PCC is made up directly from high purity of limestone. Limestone contains impurities such as silica, magnesium and others. Impurities will affect the color and the purity of limestone. So, impurities needed to be removed.

The PCC suspension can be manufactured through the process of precipitation from chemical solutions and re-carbonization of slaked lime. The high purity of limestone will undergo calcination process where it will form the formation of calcium oxide. The loss of carbon dioxide gas occurs during the calcination process.

The calcium oxide will added with distilled water to produce “milk of lime” solution and then the solution through the re-carbonization process. The synthesis of calcium carbonate widely being used around the world because of the ability to control parameters in making of fine and controlled particle size of PCC suspension.

1.2 PCC Production Technique

Based on previous studies (Dzuhri et al.; 2014), precipitated calcium carbonate (PCC) can be synthesized through two methods which are:

a) **Precipitation from chemical solutions**

A combination of mixture chemical solution is used to form precipitated calcium carbonate (PCC). The common combination of chemical solutions is the mixture of calcium chloride, NaCl and sodium carbonate, Na_2CO_3. This method is commonly used by previous researchers because it technique is in simple way and able to control the parameters with easily (Ahn et al.; 2005, Xiang et al.; 2004). As example, a research that related with this technique is the study of conversion kinetics of vaterite to calcite (Krajl et al.; 1997). The studied was carried out in aqueous solution at range from 25°C to 45°C and it has been noticed that the growth of calcite is a controlling rate process.

b) **Re-carbonization of slaked lime**

Precipitation of calcium carbonate occurs through the bubbling of carbon dioxide, CO_2 gas by using slaked lime or known as calcium hydroxide in a batch reactor. This method mostly being used in industries because the low cost and the raw materials is easier to be found. Before carried out with the re-carbonation process, calcination is needed to be done for producing calcium oxide and then water is added into the calcium oxide where it will became calcium hydroxide. (Ukrainezyk et al., 2007; Vacassy et al.; 2000).

1.3 Polymorph of Precipitated Calcium Carbonate

There are three types of crystal polymorph of calcium carbonate which are calcite, aragonite and vaterite. The common crystal that been found in calcium carbonate is calcite and aragonite. Calcite is the most stable polymorph among them. The stability of calcite made it can be used widely in many applications. Vaterite is a rare morphology and difficult to been found in limestone or marble or calcium carbonate.

Vaterite is easily transforms into calcite under extreme condition. It is the most unstable crystal morphology. Generally, raw limestone that contains vaterite crystal will undergo synthesizing process. Aragonite is the second the stable polymorph after calcite. The stability of aragonite cannot win over the calcite because the calcite crystal stable at extreme condition (high temperature and pressure) but the aragonite only stable at higher pressure.

Aragonite formed through the natural process of biological and physical whereas calcite crystal occurs by the dissolved of deposition of mineral- rich water on the walls of cliffs and caverns. Calcite crystal usually in rhombohedral shape, transparent and the color is colorless. Aragonite is not stable at higher temperature due to the structure crystal is in orthorhombic system with acicular crystals. Vaterite is in spherical shape. The formation of vaterite crystal occurs during the coal liquefaction process.

1.4 Problem Statement

Precipitated calcium carbonate (PCC) is manufactured by precipitation process via re-carbonization of calcium hydroxide, $Ca(OH)_2$ in a stirred sprayed-mist reactor during present practice. Carbon dioxide gas is bubbled back into the calcium hydroxide solution to replace the loss of carbon dioxide gas during calcination of high purity of limestone in order to produce suspension of PCC.

The bubbling carbon dioxide gas supplied into calcium hydroxide solution cannot be interrupted and must continuously supply to produce suspension of PCC. The reactor has inflexible operating controls where it is difficult to handle with rate mixing of solution, less volume production, concentration of reactant and so on. In sprayed-mist reactor, reactant needs to do in a closed chamber to manufactured finer and great surface area of PCC suspension. The key in study is to investigate the characteristics of crystal morphology of precipitated calcium carbonate (PCC) with the presence of additives during synthesis. Hence, the methods to handle with equipment must be doing in correct way.

During calcination process, a silica gel and grease was being used in desiccator where silica gel used to remove carbon dioxide gas and water vapour whereas grease used to avoid air from outside entering the desiccator. In re-carbonization process, calibration of pH meter is very important to get accurate reading of pH levels of initial reactant. In conclusion, all the steps must do with properly.

1.5 Objectives

The main objective of this project is to investigate the characteristics of crystal morphology of precipitated calcium carbonate (PCC) with the presence of additives during synthesis. In this study, the research objectives can be divided into two main areas:

1) To investigate the effect of different parameters such as concentration of calcium hydroxide, pH of reactants, flow rate of carbon dioxide gas and types of additives.
2) To study the characteristics of precipitated calcium carbonate with two different additives, EDTA and polyvinyl alcohol

1.6 Scope of Work

Chapter 2 contains the background information about mineralogy of calcium carbonate, methods to produce PCC and characteristics of PCC. The effects of parameter to control in order to manufacture synthesis of calcium carbonate from previous studies also have been mentioned here. Chapter 3 describes how the process occurs from how the high purity of limestone is transforms until it changed to calcium hydroxide solution for synthesis process. The instruments that were being used in this project also have been described in Chapter 3. The operating variable and other parameters that control the synthesis of PCC is explained and presented in Chapter 4. All the results obtained also were discussed in here. Lastly, the suggestion and conclusion to summarize about PCC for future work were explained in Chapter 5 and was followed by references and appendices.

CHAPTER 2

LITERATURE REVIEW

2.1 Calcium Carbonate, $CaCO_3$ mineralogy

Limestone is a sedimentary rock where it bearing of calcium carbonate in the form of mineral calcite. Calcite and aragonite are the mostly formed in nature of crystal morphology of calcium carbonate which is in a rhombohedral and orthorhombic crystal system state (Table 2.1, De Villiers, 1971; Redder and Markgraft, 1985) while vaterite is the rare of crystal morphology that occur in nature where the crystal system is either in hexagonal or orthorhombic (Kamhi, 1963; Le Bail et al., 2011; Medeiros et al., 2007; Meyer, 1960; Wang and Becker, 2009). Calcite it is the most stable polymorph of calcium carbonate among three of them where calcite is stable under atmospheric pressure and at room temperature condition whereas vaterite is the least stable crystal polymorph.

Aragonite is the crystal morphology at high pressure and less temperature while vaterite is stable at low temperature and pressure. The calcium mineral which is calcite, aragonite and dolomite is making up approximately 15% of the Earth's sedimentary rock. The three crystalline form minerals only can be exists under the extreme experimental conditions.

i. Calcite

- Calcite is commonly found in sedimentary, metamorphic and igneous rock where calcite is the main constituents of limestone and marble rocks. The special properties of calcite make it widely can be used in many industries.

ii. Aragonite

- Aragonite also the common crystal of carbonate mineral that forms in limestone rocks or marble around the world. The formation of aragonite occurs through biological and physical process. The processes are precipitation of calcium carbonate from marine and freshwater environments.

iii. Vaterite

- Vaterite names is comes from the name of Germany mineralogist, Heinrich Vater. Vaterite is made up from two different crystallographic structures that exist together with a pseudo-single crystal.

The crystal structures of all three of them are characterized by the shape of calcium ions. Dolomite has the same crystal structure as calcite where the structure is characterized by the alternating 6-fold coordinated calcium ions with layers of carbonate ions but dolomite always changing their calcium layer to magnesium layer for every second. The structure of aragonite is characterized by 9-fold coordinator while vaterite structure by 6 or 8 –fold coordinated in a hexagonal sub-lattice. The structure of vaterite is the least dense among them and the structure of aragonite is closely packed and denser than the structure of calcite.

Table 2.1: Mineralogical and solubility information for calcium carbonate phases (Kamhi; 1963, Tang et al.; 2009).

Mineral name	**Chemical formula**	**Crystal system**	**Crystal system (Å)**	**-log *Ksp* (at 25°C)**
Dolomite	$CaO.5MgO.5CO_3$	Rhombohedral	a = 4.8079 c = 16.010	8.55
Calcite	$CaCO_3$	Rhombohedral	a = 4.9900 c = 17.061	8.48
Aragonite	$CaCO_3$	Orhorhombic	a = 4.9614 b = 7.9671 c = 5.7404	8.34
Vaterite	$CaCO_3$	Hexagonal	a = 4.13 c = 8.49	7.73

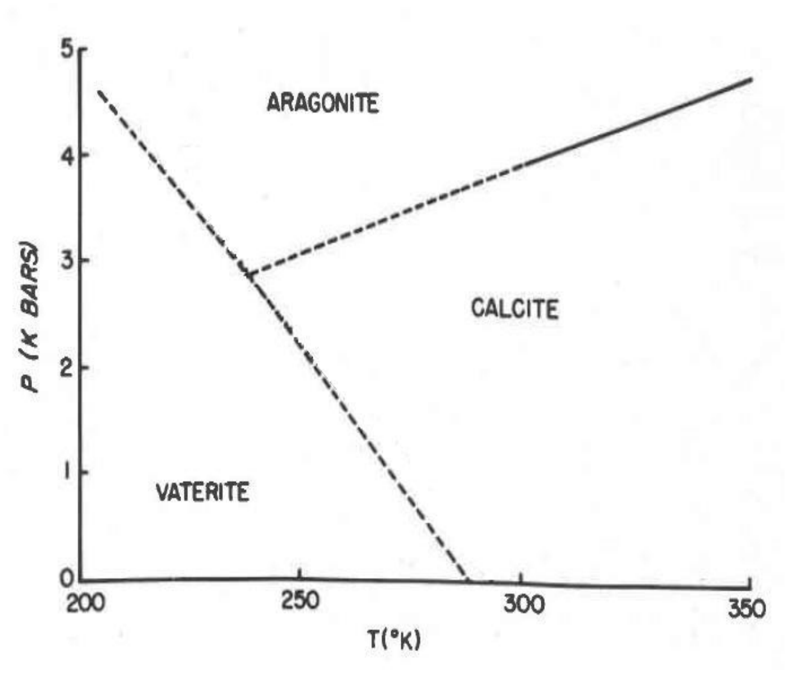

Figure 2.1: The phase diagram of calcite, aragonite and vaterite at different temperature(°K) and pressure(K bars)

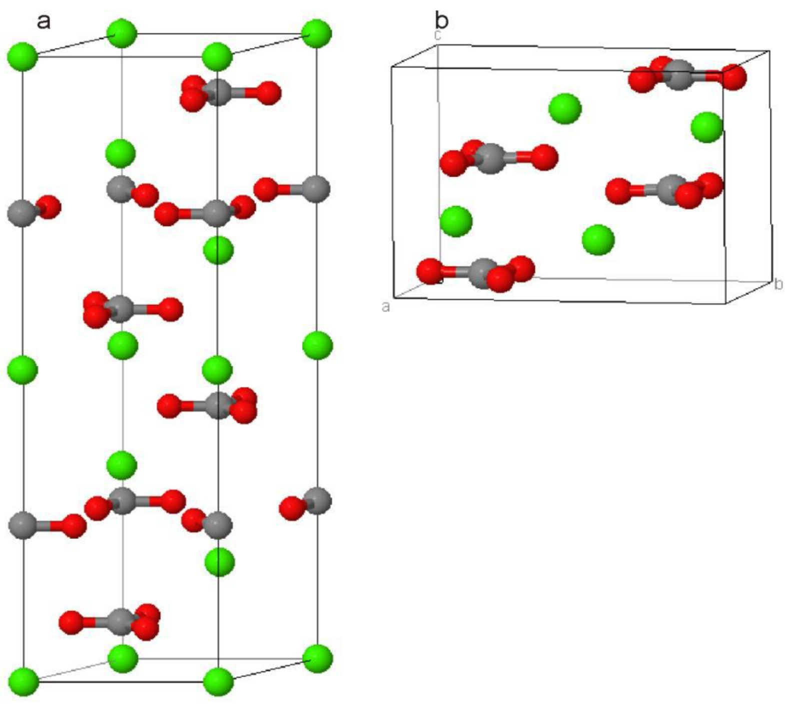

Figure 2.2: The crystal structure of (a) calcite and (b) aragonite using the crystal systems described in Table 2.1 where the green spheres represent calcium, grey spheres as carbon and red spheres as oxygen and the thin lines represent the unit cell edges.

2.2 Precipitated of Calcium Carbonate (PCC)

Precipitated calcium carbonate (PCC) or also known as purified or refined or synthetic calcium carbonate is an innovative product where it was being derived directly from high purity of limestone. The PCC was produced under the certain conditions in order to obtain crystals in proper shape, size and physical characteristics. Technically, crystal shape and size particles plays important role during synthesis of PCC.

Concentration of calcium hydroxide, $Ca(OH)_2$ or known as "milk of lime", pH of reactants, the rate flow of carbon dioxide (CO_2) gas, additives and temperature (Feng et al. ;2007) were being used as parameter to see the changing in the characteristics of PCC where the results can be seen through the particle size, shape and the grades coating of calcium carbonate.

It has been proved experimentally that the increasing the degree of concentration of calcium hydroxide, $Ca(OH)_2$ will affected the crystal morphology of PCC where it changing the shape of crystal morphology. The final analysis result of mineralogical of PCC show that the PCC have a vary size of crystals in the different temperature in presence of same additives. Additives such as EDTA and PVA are the common additive used in research that related with PCC. The increasing the number of bubbling of carbon dioxide, CO_2 gas in the presence of additive during synthesis also will increases the size particle of PCC.

The PCC were widely being used in many applications such as additives, adhesives, plastics, rubber, paper, inks, pharmaceuticals and nutritional supplements.This is because the PCC has a very high value of purity, easy to control crystal shape and particles sizes, and the colour Of PCC is more whiteness compare to calcium carbonate (limestone) are the main causes high demand for the PCC in market.

2.3 PCC Production Methods

Two basic methods routes for preparation of PCC in this study are:

i. Solution route

- The solution that contains the mixture of calcium ions and carbonate ions in aqueous solution where both molar concentration is equal. For example, aqueous solution of $NaCl_2$ and $CaCl_2$ (Feng et al.; 2007, Wang et al.; 2006, Chen et al.;1997)

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaCl \quad (2.0)$$

ii. Re-carbonization route

- The route where carbon dioxide (CO_2) gas in bubble form is supplied to calcium hydroxide, $Ca(OH)_2$ solution(“milk of lime’’) to form calcium carbonate, $CaCO_3$ (Wang et al.;2006, Xiang et al.;2002, Garcia-Carmona et al.;2003, Ukraineyzk et al,2007).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (2.1)$$

2.3.1 Chemical solution route

The route where involves double decomposition of aqueous solutions of $CaCl_2$ and $NaCl_2$. The reason because this route often being chosen among researchers because the process variable in this route are easily to control and the operation is in simple way.

2.3.2 Re-carbonization route

The most widely methods that being used in industry field to obtain PCC. The re-carbonization route is usually be chosen as a method to synthesis of PCC are due to it cost is cheapest compare others and the ability to obtain raw materials is easy (Ukraineyzk et al, 2007). There are few steps involves in preparing of PCC as described as below:

a) Calcination

Calcination or also known as calcining process is defined as a thermal treatment process where it being applied to ores and other solid materials in the absence of air in order to bring about a thermal decomposition. The purpose of calcination process also is to remove of a volatile fraction and phase transition of solid materials.

The process usually involves at high temperature but below the melting point of materials. The calcination process maybe similar to roasting process where both needed high temperature to occur but calcination process occurs in the limited supply of air (Britannica.com) whereas roasting process is a complex gas-solid reaction takes place in between solids and the furnace atmosphere.

Calcination process occurs when the crushed limestones are decomposed into calcium oxide, CaO and carbon dioxide, CO_2 gas. The heating temperature of limestone must above 900°C for calcination process to occur. This is because the solid substances will have high porosity and good crystalline when it is fired at higher temperature.

The equation for calcination process:

$$CaCO_3 \rightarrow CaO\ (s) + CO_2(\text{gas}) \tag{2.2}$$

Quicklime or calcium oxide, CaO will be produced from limestone when the temperature is reached optimum temperature for calcination process and the carbon dioxide, CO_2 gas is released during that time. During the releasing of carbon dioxide gas, weight loss of ignition of limestone is usually implied around 40% to 44%.

The process starts where the chunks of limestone is heating at adequate temperature where in the process it will begin from the outer surface to the inner surface of limestone and the reaction occurs continuously until the process is completed. The porosity of limestone is increased at the end of process. As the end of result, it will produce a calcium oxide with high chemistry reactivity and has a large internal surface area.

b) Slaking

Slaking process is a process where the water is added into the calcium oxide to produce calcium hydroxide. This process also refers as a hydration process or lime slaking. The reaction which applied in the process is exothermic reaction. The heat of materials is released into the surrounding during slaking process. Distilled water is being used in this process. A certain amount of volume of distilled water is adding into the quicklime that was obtained from the calcination process. As the final result, calcium hydroxide solution or “milk of lime” is produced.

The equation for slaking process is:

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca\ (OH)_2\ (aq) \qquad (2.3)$$

After that, the calcium hydroxide solution was screened due to the solution suspension contains impurities and coarse grits. The impurities must be removed to avoid it from affected the result of PCC. Impurities will be found as separate particles in the hydrated lime later. All the outsider particles that have a larger size than the screen mesh will be separated off when the hydrated lime was screened (Ariffin and Mahmed, 2005).

c) Re-carbonization

High purity and high grade of limestone is required to use in the re-carbonization process. Re-carbonization is a recarbonizing process (Wang et al.; 2004) where carbon dioxide, CO_2 gas is supplied into the calcium hydroxide solution. The calcium hydroxide solution reacts with carbon dioxide when the solution is bubbling with carbon dioxide, CO_2 gas under different controlled parameters such as pH value of ‘milk of lime’’, additives, concentration of “milk of lime” and others.

The process is an exothermic reaction and the reaction occurs in this process is reversible process (Garcia- Carmona et al.; 2003, Wang et al.; 2006). The overall equation for the process is:

$$Ca(OH)_2(aq) + CO_2(gas) \rightarrow CaCO_3 + H_2O \quad (2.4)$$

Calcium carbonate, $CaCO_3$ precipitation is formed after the dissolution of carbon dioxide, CO_2 gas where the carbonate, CO_3^{2-} that generated during the dissolution of carbon dioxide, CO_2 gas is reacts with calcium, Ca^{2+} ion and hydrogen, H^+ ion will reacts with hydroxide, OH^- ion to form water, H_2O. A change in concentration of certain ions is accompanied the re-carbonization process. For example of certain ions are calcium ion (Ca^{2+}) and hydroxide ion (OH^-). The mechanism that almost same stated that the reaction was terminated until there was no pH in suspension (Seo et al.; 2005).

The time period for PCC to precipitate in re-carbonization is needed to be imposed on a system is known as the induction time, relaxation time, the nucleation time and growth time (Westin and Rasmuson;2005). The relaxation time is the period of time for the cluster distribution needed to responds with the imposed supersaturation while nucleation time is the where the necessary time for production of stable nuclei and lastly, the growth time is time needed for the nuclei to grow.

2.4 Nucleation and growth

A precipitation occurs when the solution becomes very saturated or the solute cannot dissolve anymore in solvent either in heterogeneous or homogenous. This process is known as nucleation process. The nucleation process is hard process to deal in the sequence of precipitation process. This step only will start when the energy barrier that associated with the extra surface energy of the nuclei formation is conquered.

Formation of nuclei occur when a growth of molecules, ions or atoms from solution is spontaneously associated or through the using of the surface of impurity particles which is presented in the solution. Nuclei forms will gradually grow until it formed crystallites (growth process). Crystal growth is a complex process where it occurs in two main group of elemental which takes place at the crystal – solution interface or some distance from the crystal surface (Jimenez- Lopez et. al,; 2003, Krajl and Brecevie; 2007).

The ratio between the rate of nucleation of solid cores and the subsequent growth is important in order to determine the size and number of particles. The nucleation and crystal growth is the major aspect in the grow area of nanoscale materials. The numerous and smaller particles will be produced if nucleation process occurs rapidly fast while growth process of crystallites will composed of large particles size.

The number of nuclei formed will increases if the flow rate concentration of carbon dioxide, CO_2 decreases where it produces finer particles of final product (PCC).

2.5 Properties of Precipitated Calcium Carbonate (PCC)

Precipitated calcium carbonate (PCC) is an innovative product where it synthesized from limestone. In order to obtain synthesized calcium carbonate, high purity and high grade of limestone was being chosen. PCC become high demand in market because the operating variable can be controlled where it will resulted in particle size and the color of PCC. The particle size is finer and the color of final product, PCC is more whiteness compare to the calcium carbonate. There was five main of aspects of characteristics which are related with PCC.

a) Shape of Particles

Crystal morphology of precipitated calcium carbonate (PCC) is in 3-dimension shape which is either in cubes or plates or in other words in any of several prominent shapes where it contributed many functions in making of paper.

Crystal shape of PCC in scalenohedral shape is very efficient at scattered the light and it can provide to other applications very well involving brightness and high opacity of materials. Prismatic or known as barrel shape of crystal shape of PCC is the least unorganized crystal shape (less interfere bonding in the sheet). Other morphologies like porosity or bulk of sheet is very useful are paramount which acts as binder in coating process (Specialty; 2008).

b) Surface Area of Particles

Surface area depends on the particle size but it also can affect by other factors. Surface area of particles is important in fill in plastics.

c) Surface Chemistry of PCC

A particles of PCC is mostly carried a slight of positive charge (zeta potential) which can affect the bond of PCC to the paper filter and the charge can be increased, neutralized or negative by using a selecting chemical agents. The compatibility of PCC with a many of dispersants and other chemical agents makes is very useful in industries (Song et al.; 2007).

The physical properties and chemistry of calcium carbonate in among of their polymorph is not very differing from each other. A quality of the "milk of lime" or calcium hydroxide provided by polymorphs of PCC exhibits a high chemical purity where it provided a good value and high performance in applications of paper (Gill and Haskins ; 2000, Speciality ;2008).

d) Size of Particles

The size particles of PCC can be changed based on their controlled parameter. Large size of particles provided a good of sheet bulk while the small particle size can scattered light in efficient way. Production of PCC is needed in industries because of the ability to control the particle size which is the good advantage in the making of paper (Speciality; 2008).

e) Size Distribution of PCC

For obtain maximum bulk, distribution of particles over a narrow range of sizes is needed. A particle is in closely well packed where the particles exhibit larger size distribution. It is caused the less interfere with sheet strength and interfiber bond. Intermediate size allows modified of properties performance where it cannot be accomplished by other pigments (Xiang et al.; 2002, Specialty; 2008).

2.6 Effects of Parameters

The parameters being applied in this study such as pH value of reactants, rate flow of carbon dioxide gas, concentration of “milk of lime” and bubbling time will affect the reaction in process making of synthesized calcium carbonate (PCC) and their chemical characteristics.

2.6.1 Flow rate of carbon dioxide, CO_2 gas

The flow rate of carbon dioxide, CO_2 gas will contribute to the changing of crystal morphology of PCC and their phase when rate flow of carbon dioxide gas being supplied in different condition. The dissolving carbon dioxide gas and the accumulation of ions that exists (H^+, HCO_3^-, CO_3^{2-}) will improve by increasing the rate flow of carbon dioxide gas which is resulted in increases of the supersaturation of solution.

The polymorph of vaterite will transform into calcite in the presence of high supersaturation. The high supersaturation caused the nucleation and precipitation occurs. On the other hand, calcite will transforms back into vaterite in the low supersaturation. At a low flow rate of gas, calcite is the only crystal morphology that have been observed (Ljbrecevie and Nielson; 1990, Han et al.; 2006).

The induction period of precipitation occurs is reduced when the flow rate of gas increases. This happens due to the increasing the force to make the precipitation process occurs where it is caused by the increases of rate flow of gas. Based on previous research (Agnihotri et al.; 1990), the size particles of PCC have been found that to decrease with increasing of flow rate of gas. The increasing of flow rate of gas increased shear stress effects.

2.6.2 Supersaturation of PCC suspension

Supersaturation is defined as to a solution which contains more of dissolved material than solvent where the solvent cannot be dissolved anymore by the solution in any under normal condition. The supersaturation of calcium carbonate is depends on the solid forms. All different crystal morphology has different solubility. The more increases the pH of reactants, the increases the supersaturation solution where it involves the hydrocarbonate buffer equilibrium. The hydrocarbonate increased the rate of nucleation of calcium carbonate (Yu et al.; 2004).

At fixed calcium carbonate, the supersaturation will decrease and as the same time the calcium ratio increased. From the previous studies, it have been noticed that higher supersaturation forms the formation of vaterite and aragonite (Rasmuson and Westin; 2003).

2.6.3 Bubbling time

Bubbling time is refers as to the time for bubbling reaction to completed. The crystal morphology of samples prepared at the same time of induction period is different when being applied in different operating variables like concentration of calcium hydroxide and rate flow of carbon dioxide gas. The new precipitation will be forms and the particle size will grow with the progressing of bubbling time.

2.6.4 pH of reactants

Based on early study by, the nucleation rate of PCC at high pH in range 11 and 12 is where the crystal morphology is slightly lost and the particle size is decreases (Yu et al.; 2004).This is due to the precipitation takes place in high pH faster than in low pH. The increasing of pH value as well as ratio of calcium decreased the particle size. Supersaturation is low at low pH where resulted in the large particle size (Fathi et al.; 2006).

The initial pH value of the solution really affects the crystal morphology of the particles during re-carbonization process (Cheng et al.; 2004). At the beginning re-carbonization process, the initial pH is around 12 and the particle size is in irregular shape but the pH value will drop to less alkalinity or in neutral state where the pH value is between 5 and 7. X-ray Diffraction (XRD) show all the products of PCC is consisted calcite crystal eventhough the crystal morphology is affected by pH values.

2.6.5 Stirring rate

At low stirring rate, the fine particles were aggregated and dense particles is formed while the particles loose is formed at high stirring rate (Han et al.; 2006). According to the previous study, it has been found that the rate amount of the agglomerated particles of calcite is large at low stirring rate (Kitamura et al.; 2002). It is also noticed that the mass transfer of carbon dioxide bubble gas in calcium hydroxide will improve in increasing of stirring rate (Xing et al.; 2004).

2.7 Effects of additives

An additive is a substance to add to the materials in order to improve the materials. In crystallization of calcium carbonate, it have been noticed that additives have influence on the time period for the formation of calcium carbonate crystals and nucleation of PCC. The additive is able to modify certain properties during synthesis calcium carbonate.

a) Ethylenediaminetetraacetic acid (EDTA)

In the presence of EDTA, the particle size of PCC is reduced. Based on early research by Rasmuson and Westin, it was justified that increased the concentration of EDTA will shifts the shape of particle to denser and smaller in rhombic crystals and spherical agglomerates. EDTA also have been concluded that the presence of EDTA during re-carbonization process helps to make the carbonization rate became faster or in other words accelerate the rate of carbonization (Xiang et al, 2002).

b) Poly-vinyl alcohol (PVA)

Polyvinyl alcohol influences the nucleation and crystal morphology of calcium carbonate precipitation. Based on the previous study by A. Declet, E. Reyes and O. M. Suarez (2015), aragonite will form in the presence of high concentration of polyvinyl alcohol. This happens due to the interaction between polar groups with polyvinyl alcohol molecules in resulting polyvinyl alcohol molecules accumulated the surface of polymorph.

2.8 Characterization of Final Products (PCC)

2.8.1 Scanning Electron Microscopy (SEM) Analysis

A scanning electron microscopy analysis is a direct analysis of vision of the particles of precipitation of calcium carbonate where show the images of polymorph of sample. The shape of crystal morphology that exists in calcium carbonate are rhombohedral, prismatic, scalenohedral and many more based on Speciality (2008), Ukrainezyk et al. (2007), Deng and Sun (2004) and Domingo et al. (2006).

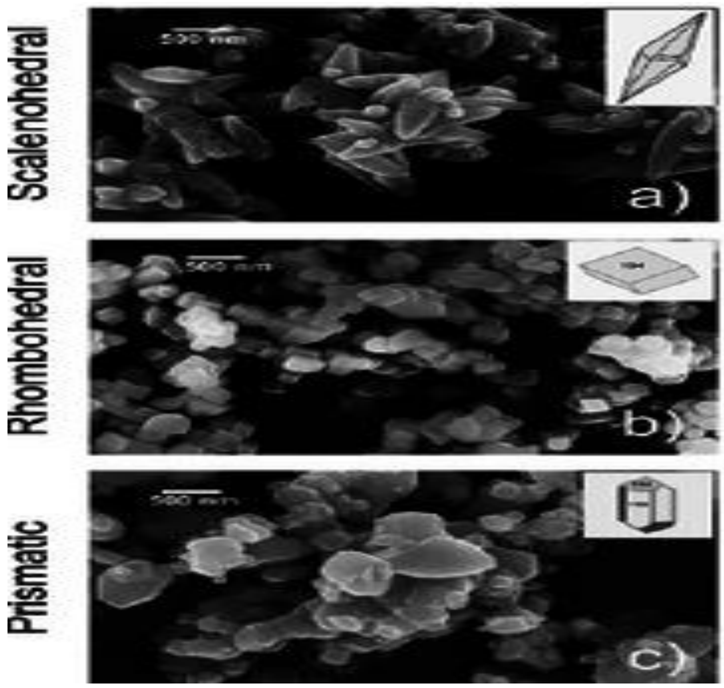

Figure 2.3: Diversities of crystal morphology of calcium carbonate

Based on Figure 2.3(a), scalenohedral is a collection of discrete particles or a cluster of individual shape which arranged in shaped of starbust pattern with many microvials. The size and shape of mineral particles in the bulk sheet can influences by the thickness of sheet.

Vaterite is the least stable crystal polymorph among three of the polymorph. Vaterite easily transforms into calcite. Prismatic calcite is a hexagonal shape (Figure

2.3(c). Prismatic calcite really helps in paper making industry where it controls the porosity of paper. A multiple of sheets will be pulled through simultaneously if the sheets are too porous (Speciality; 2008).

2.8.2 Fourier Transform Infrared (FTIR) Analysis

For calcium carbonate, infra-red spectra were recorded in the region around $400cm^{-1}$ to $4000cm^{-1}$. Aragonite shows a symmetric carbonate stretching vibration characteristics ($1083cm^{-1}$) and out-of-plane bending carbonate vibration ($854cm^{-1}$) in FTIR analysis. The out-of-plane bending carbonate vibration will cause certain characteristics shifts whereas the carbonate stretching vibration characteristics is used to determine quantify of aragonite. The comparison between three crystal morphology that exists in the formation of precipitation calcium carbonates it shown in Figure 2.4.

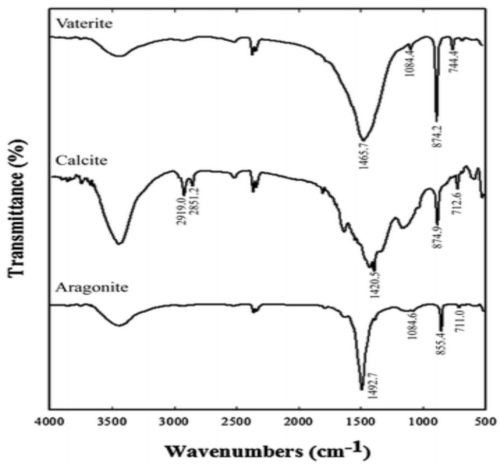

Figure 2.4: The characteristics carbonate vibrational bonds of FTIR spectra of crystal morphology calcium carbonate