

**PRODUCTION OF PRECIPITATED CALCIUM CARBONATE  
(PCC) USING MALAYSIAN LIMESTONE BASED MATERIALS  
VIA CONTINUOUS PRODUCTION TECHNIQUE**

**by**

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**Thesis submitted in fulfillment of the  
requirements for the degree of  
Masters of Science**

**April 2010**

## ACKNOWLEDGEMENTS



*In The Name of Allah, Most Gracious and Most Merciful*

Alhamdulillah, thanks to Allah s.w.t for providing me wisdom and grace to complete my research. Special thanks to my mother, Rahmah Bt Mohd Wazir, and my late father, Allahyarham Ismail Bin Bakar, for their continual and unwavering support throughout my journey to obtain a Masters degree. I humbly thank my sisters who have provided a never-ending stream of positive words towards my goals and I am very grateful for them.

Special appreciation goes to School Of Materials and Mineral Resources Engineering for providing me facilities and equipment in completing my project. I would like to express my sincere thanks to my main supervisor, Associate Prof. Dr. Kamar Shah Ariffin for his help, advice, guidance, constructive criticism and valuable suggestion during my studies, and also my co-supervisor, Dr. Norlia Baharun for her generous assistance and support.

I also want to express my appreciation to the technical staffs in the School Of Materials and Mineral Resources Engineering for their technical assistance and help. Gratitude is also expressed to Roshaida Arbain for her assistance in the research works.

A special acknowledgement is given to the Institute of Graduate Studies USM for providing me USM Fellowship throughout my studies. Not forgotten, thanks to the Ministry of Science, Technology and Innovation (MOSTI) Malaysia for funding this research under e-Science Fund (603316).

Lastly I would like to thank all my friends who helped me directly or indirectly and made my stay in USM an exciting and memorable experience.

**THANK YOU**

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## LIST OF ABBREVIATION

ASTM	American Society of Testing and Materials
BET	Brunauer, Emmet, Teller
EDTA	Ethylenediaminetetraacetic acid
FTIR	Fourier Transform Infrared Spectroscopy
HCL	Hydrochloric acid
IR	Infra red
KBr	Kalium / Potassium Bromide
LOI	Loss On Ignition
M	Molar
MOL	'Milk of Lime'
PAA	Poly acrylic acid
PCC	Precipitated Calcium Carbonate
PSA	Particle Size Analysis
SMI	Specialty Mineral Inc.
SEM	Scanning Electron Microscopes
XRD	X-Ray diffraction
XRF	X-Ray fluorescence

## LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
CO <sub>2</sub>	Carbon dioxide
CaCO <sub>3</sub>	Calcium carbonate
Ca(OH) <sub>2</sub>	Calcium hydroxide
D <sub>10</sub>	10 % volume of the particles have a size value lower than or equal to D <sub>10</sub>
D <sub>50</sub>	50 % volume of the particles have a size value lower than or equal to D <sub>50</sub>
D <sub>90</sub>	90 % volume of the particles have a size value lower than or equal to D <sub>90</sub>
g	gram
H <sub>2</sub> O	Water
L	Liter
Mt	Megatonne (1 000 000)
ρ	Density
wt%	Weight percentage

# **PENGHASILAN MENDAKAN KALSIMUM KARBONAT (PCC) BERASASKAN BATU KAPUR TEMPATAN MELALUI TEKNIK BERTERUSAN**

## **ABSTRAK**

Secara komersialnya, mendakan kalsium karbonat (PCC) dihasilkan melalui tindakbalas larutan 'susu kapur' bersama aliran gas karbon dioksida di dalam satu sistem reaktor berkelompok teraduk. Bagaimanapun, kelemahan teknik ini adalah PCC yang hendak dihasilkan tidak boleh terganggu semasa tindakbalas berlaku dan penghasilannya adalah tidak berterusan. Oleh itu, dua inovasi reaktor skala makmal telah direkabentuk iaitu tiub lurus dan reaktor semburan berkabus, digunakan dalam kajian ini untuk menghasilkan PCC secara berterusan. Matlamat utama kajian adalah untuk menganalisis kebolehan dan kecekapan kedua-dua teknik berterusan ini dengan meneliti pembolehubah pengoperasian dan parameter tertentu di samping pencirian sifat-sifat PCC yang terhasil. Batu kapur tempatan berketulenan tinggi digunakan sebagai bahan mula projek dan perlu disediakan melalui 3 proses utama iaitu pengkalsinan, penghidratan dan pengkarbonan. Keunikan proses pengkarbonan menggunakan tiub lurus terletak pada kadar alir suapannya dan tindakbalas pemendakan berlaku semasa pergerakan reaktan di sepanjang tiub yang akhirnya keluar sebagai produk (PCC) secara berterusan. Sementara itu, teknik semburan berkabus pula berupaya mengubah larutan susu kapur kepada titisan-titisan halus yang meningkatkan lagi luas permukaan reaktan untuk tindak balas pengkarbonan. Walaubagaimanapun, kedua-dua rekabentuk reaktor memerlukan set pembolehubah pengoperasian dan keadaan penganapan yang berbeza yang akan menjadi penentu kepada kejayaan proses. Tiub lurus menegak berupaya menghasilkan PCC dalam julat reaktan yang besar (0.2M hingga 1.0M) dengan kadar alir gas antara 100 hingga 600 ml/min. Manakala, reaktor semburan berkabus pula sesuai untuk menghasilkan PCC dalam julat kepekatan yang sangat rendah (0.1M hingga 0.2M) dengan penggunaan kadar alir gas yang ekstrem (>1000 ml/min). Ciri-ciri PCC seperti morfologi, saiz taburan partikel, luas permukaan spesifik dan ketulenan turut dianalisis. Keputusan menunjukkan bahawa kedua-dua teknik ini berjaya menghasilkan PCC yang berketulenan tinggi dengan pelbagai morfologi dan ciri-ciri tertentu. Penggunaan reaktor tiub lurus berupaya menghasilkan PCC dengan pelbagai morfologi berbentuk seperti kubus, prismatik serta skalenohedral dalam julat saiz antara 100 hingga 600 nm. Manakala, teknik semburan pula berupaya menghasilkan PCC dengan morfologi kristal rombohedral dalam julat saiz terhad antara 200 hingga 1500 nm. Namun, kesemua PCC yang dihasilkan adalah dalam kategori polimorf yang sama iaitu kalsit walaupun mempunyai bentuk morfologi yang berbeza. Umumnya, kedua-dua inovasi teknik penghasilan berterusan ini dilihat berupaya menghasilkan PCC dengan spesifikasi yang dikehendaki untuk pelbagai kegunaan industri dan dapat diperbaiki lagi.

# **PRODUCTION OF PRECIPITATED CALCIUM CARBONATE (PCC) USING MALAYSIAN LIMESTONE BASED MATERIALS VIA CONTINUOUS PRODUCTION**

## **ABSTRACT**

In present commercial practice, precipitated calcium carbonate (PCC) is normally manufactured by reacting the ‘milk of lime’ with carbon dioxide (CO<sub>2</sub>) in a stirred tank batch reactor system. The drawback of this technique is PCC could not be produced uninterrupted for the required quantity in a real time process continuously. Thus, two newly designed lab scale reactors i.e. tall tubular and sprayed-mist are used in this study to produce PCC in continuous mode. The main aim is to investigate the operating variables that control the PCC synthesis using these continuous techniques as well as to evaluate the properties of the resulted PCC. High purity local limestone is used as a starting material and needs to be prepared involving 3 main processes which are calcinations, slaking and recarbonation. The uniqueness of the tall tubular reactor is the feed flow rate and the recarbonation took place while suspension is moving up the tube that afterwards will discharge via the outlet continuously as products (PCC). Meanwhile, the sprayed-mist technique capable to increase the surface area of the reactant by converting ‘milk of lime’ into fine mists, thus enhanced the recarbonation process. However, the operating variable settings (reactant concentration, CO<sub>2</sub> gas flow rate and feed flow rate) are different from each technique which depends on the reactor design. Tall tubular reactor is able to cope with wide range of reactant concentration (0.2M to 1.0M) and gas flow rate between 100 to 600 ml/min. In contrast, sprayed-mist reactor is suitable to precipitate PCC at lower reactant concentration (between 0.1M to 0.2M) with the extremely high gas flow rate (>1000 ml/min). The properties of the resulted PCC like crystal morphology, particle size distribution, specific surface area and purity are also determined. The results showed that both techniques be able to manufacture higher purity of PCC successfully with various morphologies and characteristics. PCC with morphologies that varied from rhombohedral, prismatic to scalenohedral shape in the size range between 100 to 600 nm can be produced via tall tubular reactor in the predetermined setting. Meanwhile, sprayed-mist technique tends to produce PCC with rhombohedral shape/ morphology in the size range of 200 to 1500 nm. All PCC products have calcite morphology even the morphology are looked different. To conclude, these new innovations are capable to produce PCC that fulfilled the industrial requirements for various applications what can be further improved.

# CHAPTER 1

## INTRODUCTION

### 1.1 Introduction

Precipitated Calcium Carbonates (PCC) is a white, bright and synthetic product that can be produced in a variety of particle shapes (morphologies) and sizes for use as a functional additive in sealants, adhesives, plastics, rubber, inks, paper, pharmaceuticals, nutritional supplements and many other demanding applications. PCC is particularly useful in paper coatings, because it imparts good optical performance characteristics to paper resulting in a brighter, glossier more opaque paper, while also providing a high resistance to yellowing and aging (Feng et al., 2007, Cheng et al., 2004, Xiang et al., 2003, Vucak et al., 1998).

The real advantage of PCC lies in the possibilities of tailor-making the product regarding morphology, particle size and specific surface area. There are several various types of PCC grades, but the purity of PCC is usually 99% with density of  $2.7 \text{ g/cm}^3$ . As a coating pigment, the average particle size is about  $0.4\text{--}2.0 \text{ }\mu\text{m}$  with a refraction index of  $1.49\text{--}1.67$  and specific surface areas of  $4\text{--}11 \text{ m}^2/\text{g}$  was used. The high refraction index and narrow particle size distribution of PCC promotes sheet light scattering. The particle size affects paper smoothness, gloss and printing characteristics. Printing characteristics are also related to particle size distribution and shape, which also affects the consumption of chemical additives in papermaking. Meanwhile, the ISO brightness for a PCC coating pigment is 95%, which requires a very pure limestone as raw material (Brecevic and Kralj, 2007, Teir et al., 2005).



In many applications of PCC it would be advantageous to be able to use very small calcium carbonate particles, < 100nm in size, which are uniform in quality and nearly uniform in size. These types of applications are needed, for example, in the pharmaceutical, cosmetics and food industries. The paints, plastics, rubber, pigment and paper industries, including the techno-chemical industry, also find use for this type of calcium carbonate product.

## **1.2 Worldwide PCC production and consumption**

There are three market leaders in the global PCC industry which are Minerals Technologies Inc (MTI) (of the US), Omya (of Switzerland) and Imerys (of France). They account for about 40% of total world PCC capacity and for more than 90% of the capacity attributable to satellite units. MTI pioneered the concept of satellite PCC production and it still dominates this sector, with 51 units, having a combined capacity of 3.2-4.3 megatonnes/year. The other 42 satellite PCC units around the world are operated by ten other companies, notably Omya and Imerys (Pigments, 2009).

The paper industry has always been the largest end-use sector for PCC. This remains the case today, with the paper industry accounting for about 40% of global PCC consumption – 5.5 Mt, including 1.8 Mt in Asia, 1.6 Mt in Europe and 1.5 Mt in North America (Pigments, 2009). The use of PCC in paper is forecast to rise by an average of 5% a year and reach 7.2 Mt by 2010. Overall demand for PCC is forecast to rise from 7.75 Mt in 2004 to 9.7 Mt by 2010, an average rise of around 4.4% per year (Roskill, 2008).

In Malaysia, Specialty Minerals Malaysia Sdn. Bhd., has constructed a satellite precipitated calcium carbonate (PCC) plant at a paper mill owned by Sabah Forest Industries Sdn. Bhd. at Sipitang, Sabah in 2003. The plant represent capacity equivalent to 25,000 to 35,000 tons of PCC produced annually (Goliath, 2008).

Chinese PCC consumption is forecast to rise by 6% per annum to reach 8 Mt by 2012, which will represent one-half of total world consumption by then. Consumption in the world as a whole is forecast to rise by 4% per annum from 13 Mt in 2007 to 16 Mt in 2012. This is a far cry from the 15% per annum growth experienced in the late 1980s and early 1990s, but it is still a respectably healthy rate of growth for any pigment nonetheless (Pigments, 2009).

In the United States, PCC has been experiencing a growth surge since 1986, attributable to the paper industry's conversion from acid papermaking technology to alkaline and to the success of the PCC on-site satellite plant concept where producers supply product from plants located adjacent to paper mills (Schlag, 2007).

Traditionally, PCC was used only as a filler, but demand has been rapidly increasing for coating grades of PCC (or PCC/GCC blends). The main application for filler-grade PCC is in woodfree uncoated paper, representing 40% of total world printing and writing papers consumption (Pigments, 2009).

### 1.3 PCC Production Technique

In the previous studies, PCC can be synthesized by two methods which are:

- (i) Precipitation from aqueous solutions (liquid-liquid-solid) – to form  $\text{CaCO}_3$  using chemical combination which is a mixture of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and calcium chloride ( $\text{CaCl}_2$ ). This method is often adopted in a laboratory study, because of its simplicity in the operation or its easiness in controlling process variables (Xiang et al., 2004, Ahn et al., 2005). For example, Krajl et al. (1997) studied the conversion kinetics of vaterite to calcite in aqueous solutions at 25 – 45 °C and found that the growth of calcite was the rate-controlling process. Kitamura et al. (2002) revealed the effect of the supersaturation, the mixing rate of the reactant solutions and temperature on the morphology and the crystallization of polymorphs in  $\text{CaCl}_2 - \text{Na}_2\text{CO}_3$  aqueous solutions and found that the precipitation behavior and the morphology change were related to the formation of the precursors.
- (ii) Carbonation of slaked lime (gas – liquid – solid) – to precipitate  $\text{CaCO}_3$  by bubbling  $\text{CO}_2$  gas through slurry of  $\text{Ca}(\text{OH})_2$  in a batch reactor is usually used in industry due to its low costs and the availability of raw materials. This process often includes the calcination of the limestone to produce quicklime ( $\text{CaO}$ ) which is then purified separately before recombining for  $\text{CaCO}_3$  precipitation (Feng et al., 2007, Ukrainczyk et al., 2007a, Vacassy et al., 2000).

## 1.4 Problem Statement

In present day practice, Precipitated Calcium Carbonate (PCC) is normally manufactured by precipitation process reaction via recarbonation of ‘milk of lime’ ( $\text{Ca}(\text{OH})_2$ ) in a stirred tank batch reactor system. Carbon dioxide gas resulted from calcinations of highly purity limestone tapped in a lime kiln is bubbled back into the ‘milk of lime’ in the reactor to generate PCC suspension.

The drawback of batch-wise technique is PCC could not be produced uninterrupted for the required quantity and specific products characteristics in a real-time process continuously. These specific products characteristics are crystallite morphology, particle size range, surface area, size uniformity, brightness etc. In batch-wise method such products characteristics could also be produced by varying and optimizing the operating conditions and other parameters. However, batch-wise technique offer less flexible operating controls such as to cope with wide range reactant concentrations, mixing rates, small production volume, spontaneous reaction production (short resident time), better reactant product separation etc.

Innovative PCC production via continuous reactor designs is an alternative to this current practice should be endeavoured. Two continuous production process techniques are possible either as a “flowing stream” of reactants fed into the reactor (tubular tube) and emerge as continuous stream of product and via “sprayed-mist” technique. In sprayed-mist technique, the reactant needed to be converted into mist/reactant droplets in a closed chamber to create greater surface area for spontaneous reaction for finer (nanoscale) and continuous product formation. The key research of this project initiative is to study and experiment the possibility to manufacture PCC in

continuous modes using both proposed techniques. The performances of these techniques rely in the design features of these reactors and the ability of the techniques to produce the desired PCC characteristics successfully.

## **1.5 Research Objectives**

The main objective of this research project is to explore new approaches in the techniques and process for Precipitated Calcium Carbonate (PCC) manufacturing other than conventional practice via batch-wise methods. In this research, emphasis is given on the continuous-wise process based on specific continuous-reactor types designed in-house.

Amongst the main related research activities and focus are:

- To design a cost effective and practical laboratory reactors scale for PCC production via continuous flow production concept – Tall tubular and sprayed-mist type reactors.
- To apply and experimenting such potential continuous reactors techniques in PCC production.
- To investigate the controlling factors (operating variables and other parameter conditions) those control the PCC synthesis using these techniques.
- To evaluate and determine the PCC properties (crystal morphology, particle size, agglomeration, brightness, etc.) which are key important indicators of PCC quality produced based on these techniques and industrial requirements.

## **1.6 Outline of the thesis**

Chapter 2 contains background information about PCC, methods to synthesis PCC, characteristics of PCC product and applications of PCC in industry. The effects of the operating variables to the PCC synthesis from the previous research are also mentioned here. Chapter 3 describes the procedures for reactant ('milk of lime') preparation prepared from the raw material (limestone) and methodology of the newly proposed techniques for continuous PCC production. Brief explanations about the equipments used for PCC product characterization are also given here. In Chapter 4, the operating variables and other parameter conditions that control the PCC synthesis are presented and the settings for optimum continuous production using both techniques were determined. The properties of PCC products that had been produced using these new techniques are evaluated and discussed accordingly. Finally, conclusions that wrap up the findings and suggestions for future work are given in Chapter 5, followed by references and appendices.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Precipitated Calcium Carbonate

Precipitated calcium carbonate (PCC) is synthesized by modifying the morphology of calcium carbonate and using the compound that has a calcium and carbonate radical. The current PCC production uses mined, crushed calcium carbonate as raw materials. Due to its properties such as uniform shape and size, which are more effective than any other type  $\text{CaCO}_3$ , the application of PCC are diversity (Seo et al., 2005, Vucak et al., 1998).

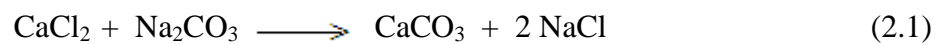
PCC find use in a broad range of manufactured and consumer products ranging from paper and paper coatings to plastic and elastomer reinforcement to food supplements and cosmetics. Calcium carbonate is particularly useful in paper coatings, because it is relatively inexpensive and imparts good optical performance characteristics to paper resulting in a brighter, glossier more opaque paper, while also providing a high resistance to yellowing and aging (Cheng et al., 2004).

The application of  $\text{CaCO}_3$  particles is determined by a great number of strictly defined parameters, such as morphology, structure, size, specific surface area, brightness, oil adsorption, chemical purity and so on. It is often desired to produce PCC in specific forms and particle sizes such as the small particle size calcite form. For each end use there exists a tailor-made product, where fineness and particle size distribution are optimally balanced to meet the technical demands of that particular requirement (Han et al., 2006, Park et al., 2008b, Xiang et al., 2002).

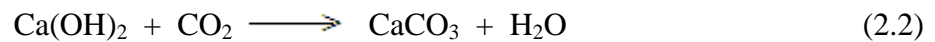
## 2.2 Method of PCC Synthesis

In the literature, two basic synthetic routes to prepare PCC are:

- (i) the *solution route*, wherein mixing the solutions containing calcium ion and carbonate ion especially in aqueous  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  system in an equimolar ratio (Wang et al., 2006, Feng et al., 2007, Chen et al., 1997).



- (ii) the *carbonation route*, in which  $\text{CO}_2$  gas is bubbled through an aqueous slurry of  $\text{Ca}(\text{OH})_2$  to form  $\text{CaCO}_3$  (Ukrainczyk et al., 2007a, Wang et al., 2006, Garcia-Carmona et al., 2003a,b, Xiang et al., 2002).



### 2.2.1 Solution Route

The solution route which involves double decomposition of aqueous solutions of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  is often adapted in a laboratory study because of its simplicity of operation or its ease in the control of process variables. Amongst of the experiments from the previous researchers are described as follows:

- i. Cheng et al. (2004) have prepared monodispersed cubic  $\text{CaCO}_3$  particles by treated solution of  $\text{CaCl}_2$  with  $\text{Na}_2\text{CO}_3$  in water in the presence of PAA at  $80^\circ\text{C}$ .



- ii. Wang et al. (2001) synthesized aragonite whiskers by using solution route in the presence of PEG as surfactant where temperature was maintained at 90°C until completion of the reaction under constant stirring.
- iii. Ahn et al. (2005) synthesized single phase aragonite PCC using Ca(OH)<sub>2</sub> slurry and Na<sub>2</sub>CO<sub>3</sub> solution in the reactor with diameter of 10cm and a volume of 1.0L which conducted at 75°C under constant agitation speed of 400rpm.

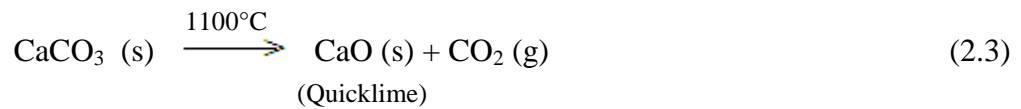
### **2.2.2 Carbonation Route**

The carbonation route is the most widely used method to obtain PCC in the industrial scale. This is due to the availability of raw materials and their low costs (Ukrainczyk et al., 2007a,b). Basically, the industrial procedure of preparing PCC consists of three steps:

#### **(a) Calcination**

Calcination (also referred to as calcining) is a thermal treatment process applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. Calcination is to be distinguished from roasting, in which more complex gas-solid reactions take place between the furnace atmosphere and the solids; however, calcination takes place in the absence of air (Wikipedia, 2008).

Calcination is an equilibrium reaction. In principle,  $\text{CaCO}_3$  will decompose to lime if the ambient partial pressure of  $\text{CO}_2$  is below the equilibrium value of the partial pressure at a given time. Conversely, any lime formed will transform back to carbonate if the partial pressure of  $\text{CO}_2$  exceeds this equilibrium value. The rate of the decomposition reaction will thus be governed by the partial pressure of  $\text{CO}_2$ , the reaction temperature and the particle size. At  $700^\circ\text{C}$  and atmospheric pressure, the rate of the reaction becomes exceedingly slow, even in the absence of  $\text{CO}_2$ . The chemical reactivity is known to vary between sources, not only because of the differences in crystalline structure, but also depending on the nature of the impurities. Equation 2.3 is the chemical reaction for calcinations (Teir et al., 2007, Ariffin, 2000).

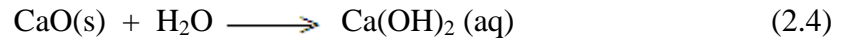


The evolution of the dissociation completion was performed by measuring the mass loss of the samples before and after calcinations. The mass loss corresponds to the released amount of  $\text{CO}_2$  during the calcination process. The measured percentage of mass loss is around 44 % (Moropoulou et al., 2001).

**(b) Slaking**

Slaking is the method for hydrating calcium oxide ( $\text{CaO}$ ) with an aqueous slaking medium which usually is distilled water changing the state from solid to a hot milky white slurry or better known as slaked lime or ‘milk of lime’ ( $\text{Ca(OH)}_2$ ). The

hydration of CaO is a non reversible and highly exothermic reaction (with temperatures up to 100°C).

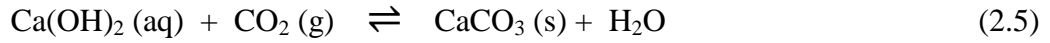


The resulting ‘milk of lime’ suspension normally contains numerous amounts of fine hydrated lime crystal is subsequently screened to remove coarse grits and to minimize impurities. Impurities in the burnt lime, such as clay or silicate particles, or residual calcium carbonate will in general not be affected by the slaking process. These kinds of impurities will afterwards be found as separate particles in the hydrated lime. When the hydrated lime was screened, all the foreign particles having a larger size than the screen mesh will be separated off (Ariffin and Mahmed, 2005).

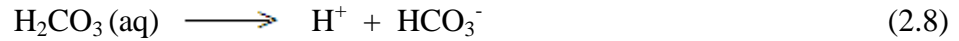
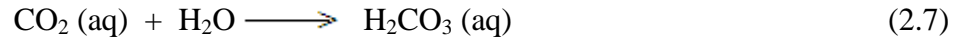
Meanwhile, Moropoulou et al. (2001) has stated that two simultaneous phenomena are observed during the hydration of quicklime which are the increment of temperature (exothermic reaction) and expanded of the paste’s volume.

### (c) **Carbonation**

The carbonation process requires the use of high purity lime and therefore high-grade limestone. Carbonation process occurs when CO<sub>2</sub> gases is bubbled through milk of lime suspension (Ca(OH)<sub>2</sub>) under various controlled parameters. The carbonation of Ca(OH)<sub>2</sub> is exothermic but this reaction is reversible (Wang et al., 2006, Garcia-Carmona et al., 2003a). The overall process of the carbonation is presented by the equation 2.5.



The reactions involved in the carbonation are listed below:



The mechanism sequences involved in the recarbonation is the dissolution of  $\text{CO}_2$  gas in the form of  $\text{H}_2\text{CO}_3$  and then converted to  $\text{H}^+$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions [eq.2.7 & 2.8]. After the dissolution of  $\text{CO}_2$ , the generated  $\text{CO}_3^{2-}$  ion through equation (2.7 & 2.8) and (2.9) reacts with  $\text{Ca}^{2+}$  ion and formed  $\text{CaCO}_3$  precipitate immediately and  $\text{H}^+$  with  $\text{OH}^-$  to form  $\text{H}_2\text{O}$  (Ryu et al., 2007, Han et al., 2005, Wen et al., 2003).

The carbonation process is accompanied by a change in concentration of certain ions, especially  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions; the carbonation process was therefore monitored by determination of the system conductivity. The similar mechanism also reported by Seo et al. (2005) which stated that the reaction was ceased until there were no variations of conductivity and pH in suspension.

According to Westin and Rasmuson (2005), the time period necessary for PCC to precipitate in recarbonation has been imposed on a system is commonly referred to as the induction time. The induction time consists of three distinguishable time periods: the

relaxation time, the nucleation time and the growth time. The relaxation time is the period of time the cluster distribution needs to respond to the imposed supersaturation. The nucleation time is the time needed for the production of stable nuclei. The growth time is the time necessary for the nuclei to grow.

A conclusion of the precipitation process is illustrated in Figure 2.1 (Wei et al., 2003). After the dissolution of  $\text{CO}_2$ , the freshly formed  $\text{CO}_3^{2-}$  reacts with  $\text{Ca}^{2+}$  and forms the temporary resultant of amorphous calcium carbonate, which is an unstable form and often described in spherical shapes of diameter lower than  $1\ \mu\text{m}$ . The initially formed  $\text{CaCO}_3$  is quickly transformed within a few minutes to two crystalline phases and followed by phase transformation from spherical vaterite to rhombic calcite. The transformation takes place through the dissolution of vaterite and follows by the crystallization of calcite

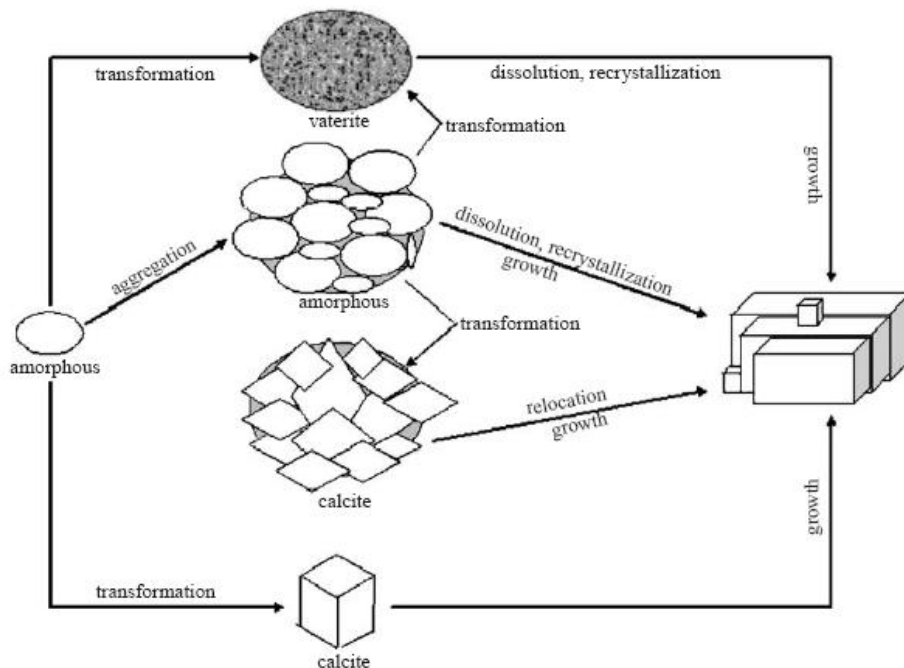


Figure 2.1: Schematic depiction for the formation of  $\text{CaCO}_3$  (Wei et al., 2003)

The calcite synthesized through the carbonation in a  $\text{Ca}(\text{OH})_2$  suspension is a typical example of the reactive crystallization. The  $\text{CaCO}_3$  molecules generated instantaneously in equation 2.11 may colloid with each other and overcome a Gibbs free-energy barrier to reach a critical size to form nucleus. The process is driven by the difference in Gibbs free energy of  $\text{CaCO}_3$  molecules between the solution and crystal phase. Nucleation and the subsequent crystal growth of calcium carbonate depend on the level of supersaturation generated from the chemical reaction. The reactive crystallization process often involves dissolution of  $\text{Ca}(\text{OH})_2$ , gas-liquid mass transfer of  $\text{CO}_2$  and chemical reaction steps. Figure 2.2 illustrates the gas-phase and liquid-phase concentration profiles that one may find in the carbonation of  $\text{Ca}(\text{OH})_2$  suspensions during the reactive crystallization (Lin et al., 2006).

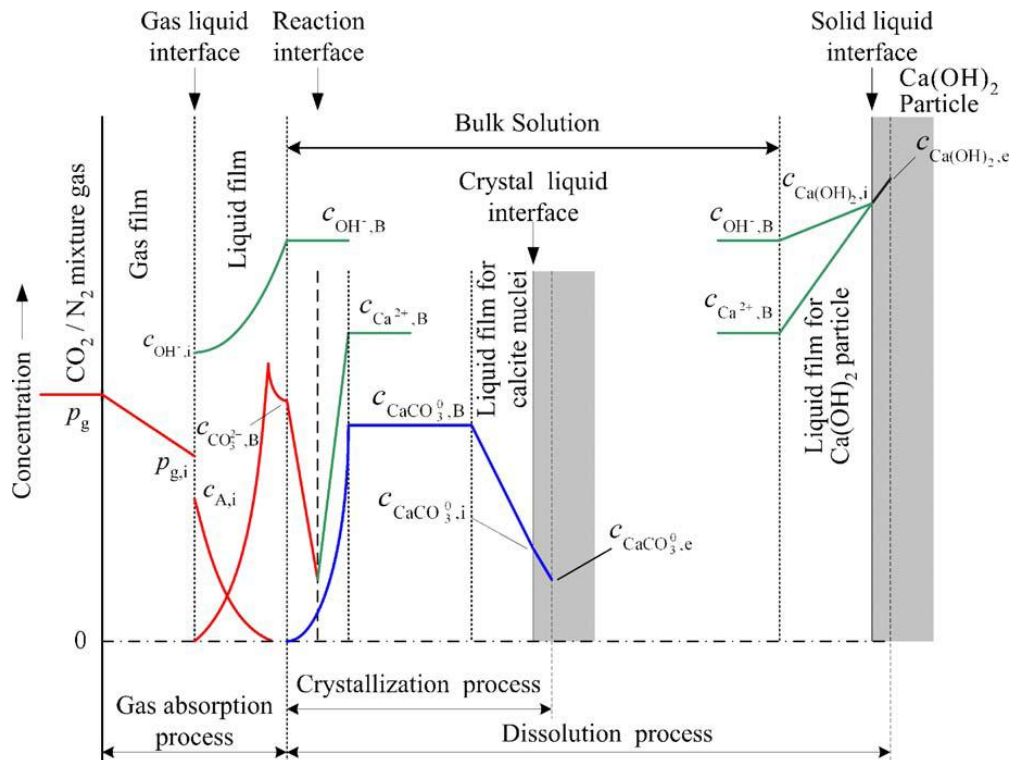


Figure 2.2: Concentration profiles for the components in gas and liquid phases in the reactive crystallization (Lin et al., 2006)

## **2.3 Categories of reactor**

Systems in which chemical reactions take place are called reactors. There are many types of reactors that can be divided into two broad categories, batch reactors and continuous reactors. Usually, batch reactor is preferred to be used in the industry for PCC production.

### **2.3.1 Batch Reactor**

Batch reactors are stirred tanks sufficiently large to handle the full inventory of a complete batch cycle. The stirring of the contents of the tank is affected by an agitator which is mounted on a shaft inserted through the vessel lid. Batch reactors are very versatile and are used for a variety of different unit operations (batch distillation, storage, crystallisation and liquid-liquid extraction) in addition to chemical reactions. There is a large installed base of batch reactors within industry and their method of use is well established. Batch reactors represent an effective and economic solution for many types of slow reactions (Wikipedia, 2008a, Wojciechowski and Rice, 2003).

Based on the previous studies, batch wise method is frequently employed in the PCC production. The designs of the reactors that have been used by previous researchers are as follows:

- i. Montes- Hernandez (2007) used a titanium reactor (autoclave with internal volume of 2L) where the dispersion of  $\text{Ca}(\text{OH})_2$  were carried out inside the reactor and heated at  $90^\circ\text{C}$  with heating system adapted to the reactor together with the injection of  $\text{CO}_2$  gas.

- ii. Chakrabarty and Mahapatra (1999) have used stirred tank reactor with internal diameter of 27cm and consists two impeller with diameter of 10cm. Aqueous  $\text{CaCl}_2$  added at a feed rate of 90 mL/min to  $\text{Na}_2\text{CO}_3$  and the temperature was maintained at 32°C.
- iii. Domingo et al. (2006) used a thermostated double-wall Pyrex atmosphere reactor of 2.2L capacity provided at a vertical shaker. Precipitation was carried out by bubbling a mixture of  $\text{CO}_2:\text{N}_2$  at flow rate of 7.5L/min.
- iv. Feng et al. (2007) used glass reactor (a cylindrical container) with a porous frit at the bottom to support the  $\text{Ca}(\text{OH})_2$  solution in the container while allowing  $\text{CO}_2$  gas pass through.

### 2.3.2 Continuous Reactor

As their name implies, continuous reactors (alternatively referred to as flow reactors) carry material as a flowing stream. Reactants are continuously fed into the reactor and chemical reaction takes place while the reactant mixture flows through and emerge as continuous stream of product (Wikipedia, 2008a).

The rate of many chemical reactions is dependent on reactant concentration. Continuous reactors are generally able to cope with much higher reactant concentrations due to their superior heat transfer capacities. Plug flow reactors have the additional advantage of greater separation between reactants and products giving a better concentration profile. The small size of continuous reactors makes higher mixing rates



possible. The output from a continuous reactor can be altered by varying the run time that consequently will increase operating flexibility (Wikipedia, 2008a).

The size of reactor for a purposed feed rate depends on the reaction kinetics of the materials undergoing chemical change and on the flow conditions in the reactor. The flow conditions are determined by the cross sectional area of the path through which the reaction mixture flows; i.e. on the shape of the reactor. Thus, it is apparent that size and shape are interrelated factors, which must be taken together when considering the continuous reactors.

However, the continuous techniques for PCC production are very scarce to be found in the literature because the difficulty to control the precipitation process but two continuous reactors that have used in these studies are discussed as follows:

**(a) Tubular Reactor**

The tubular reactor is a reactor in the form of a cylindrical tube through which feed / reactant flowing in and product exists at the other end. In the tubular flow, the residence time in the reactor is the same for all elements of fluid, i.e., the reaction proceeds as the reactants in a tubular progress along the reactor tube. The chemical reactions take place in a stream of gas that carries reactants from the inlet to the outlet. Mass and energy transport occur through a convection-diffusion and convection-conduction processes (Gilmour and Samson, 2000).

A narrow residence time distribution can be achieved by turbulent flow conditions in the tubular reactor. In case of small tube diameters, the geometry allows operation at high pressures. The favorable ratio of surface to volume enhances heat transfer and thus simplifies the adjustment of a desired axial temperature profile. These advantages make the turbulently operated tubular reactor with small diameter the most recommendable continuous reactor type (Stahl et al., 2003).

For the vertical tubular reactor, the reactant and gas bubbles are injected from the bottom to fill up the reactor. Due to buoyancy, the bubbles rise inducing a circulating motion of the liquid. Furthermore, as the bubbles rise through the suspension/liquid, gas dissolves from the bubbles into liquid (Richardson and Peacock, 1994).

Meanwhile, Vacassy et al. (2000) have synthesized PCC continuously using a new segmented flow tubular reactor (SFTR). There are two main parts of SFTR which are a mixer and a tubular reactor. The functions of the mixer are to mix thoroughly the reactants and to segment the liquid reaction mixture into small identical section. The tubular reactor which used PTFE tubes with 4 mm of inner diameter and 10 m of length is the part where the reaction progresses to produce PCC. The mixer is placed on the upstream side of the reactor setup while the tubular reactor is placed on the downstream side. The reactants are fed into the setup by means of the peristaltic pump. Several precipitation methods likes solution and carbonation route were tested successfully using this reactor.

## **(b) Sprayed-mist reactor**

Sprays are used to deliver specific liquid atomization characteristics, liquid spatial distribution and impact (as including applications) as well as to cool and condition process gases but this type of reactor is not commonly used in the industry especially in PCC production.

There are several methods for atomization of mists. The ultrasonication method is available for production of fine mist. The atomization units commonly used for spray drying are fluid phase spraying nozzles, high pressure nozzles, and centrifugal atomizations. The sizes of mists and particles usually become large when high pressure nozzles are used. However, some nozzles are not suitable for spraying a suspension because of abrasion (Hino et al., 2000).

In the sprayed-mist reactor, the spraying apparatus is typically fitted at the top section of the precipitation reactor to disintegrate the mist of reactants to react with gas. Rapid mixing of the mist into the gas enables a very short effective reaction time and thus a very short production time for the product (Maijala et al., 2006).

## **2.4 Polymorphs of PCC**

Calcium carbonate exists in one of three different *polymorphs*, or spatial arrangements, of its calcium and carbonate ions. Calcium carbonate polymorphs are *calcite*, *aragonite* and *vaterite* (Park et al., 2008, Specialty, 2008, Huang et al., 2007). All these polymorphs are observed in nature, and can be produced from processes that yield synthetic precipitated calcium carbonate, or PCC. The illustration for various polymorphs of PCC can be seen at Figure 2.3 (page 41).

### 2.4.1 *Calcite*

Calcite is thermodynamically most stable form of calcium carbonate at room temperature and at atmospheric pressure and should therefore eventually form. Calcite has a trigonal crystalline form with crystal habits such as scalenohedral, rhombohedral, hexagonal prism, pinacoid, and cubic, and prismatic. These particular morphologies are important because the coating properties, such as light scattering, of a calcium carbonate material are strongly correlated to its morphology and particle size. Prismatic and rhombohedral-shaped PCC have maximum light scattering at 0.4 to 0.5  $\mu\text{m}$  sized particles, while scalenohedral-shaped PCC has maximum light scattering of 0.9 to 1.5  $\mu\text{m}$  particles. The aforementioned small-shaped sized, rhombohedral morphology makes the material particularly effective for use in a paper coating composition (Brecevic and Kralj, 2007, Kuriyavar et al., 2000, Naka et al., 2000).

Calcite has a rhombohedral crystal structure with space group  $R\bar{3}c$  and  $a = b = 4.990 \text{ \AA}$ ,  $c = 17.061 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$  (Garcia-Carmona et al., 2003a,b, Leeuw and Parker, 1998).

In rhombohedral and/or hexagonal calcite, the  $\text{CO}_3^{2-}$  sub-lattice is hexagonal and the triangular  $\text{CO}_3^{2-}$  ions are coplanar. The planes containing  $\text{CO}_3^{2-}$  ions are perpendicular to the c-axis and they are rotated by  $60^\circ$  from one  $\text{CO}_3^{2-}$  layer to the next (Kuriyavar et al., 2000).

The rhombhohedral form is particularly effective in imparting good optical performance (e.g., increasing the light scattering coefficient). Furthermore, it has been noted that for PCC having a rhombohedral morphology, there is an inverse relationship

(within certain particle ranges) between optical performances and particle size – smaller particle sizes leads to better optical performance. Additionally, it is preferred that this PCC have a narrow particle size distribution that results in a paper or coating structure that is a more efficient scatter of light and thus imparts enhanced optical performance properties, particularly opacity and gloss to paper products (Domingo et al., 2006, Cheng et al., 2004).

#### **2.4.2 Aragonite**

The aragonite polymorph generally exhibits needle-shaped orthorhombic crystals structure with space group *Pmcn* and  $a = 4.8314 \text{ \AA}$ ,  $b = 7.8359 \text{ \AA}$ , and  $c = 5.7911 \text{ \AA}$  while  $\alpha = \beta = \gamma = 90^\circ$  (Leeuw and Parker, 1998, Qingfeng et al., 1998). The needle shape is called acicular, and the ratio of length-to-diameter of the crystals is called aspect ratio. High aspect ratio aragonite is useful in many applications (Wang et al., 2004).

In paper coatings, this morphology tends to produce high gloss finishes and is better at covering substrates at lower coating thicknesses. A high aspect ratio also can improve strength or impact resistance in polymeric materials that employ this form of calcium carbonate as an additive. Sometimes, clusters of needle-shaped crystals are observed, and these can be very efficient at scattering incident light (Park et al., 2008a, Ahn et al., 2005, Wang et al., 2004).

In the aragonite structure, although the  $\text{CO}_3^{2-}$  sub-lattice is hexagonal, the disposition of the  $\text{CO}_3^{2-}$  ions with respect to  $\text{Ca}^{2+}$  ions is different. A general trend toward aragonite was found at higher temperature. Aragonite has a slightly higher density than calcite and is also slightly more soluble (Kuriyavar et al., 2000).

Aragonite is one of the less abundant crystalline polymorphs of  $\text{CaCO}_3$  and it is metastable. It is formed under a narrower range of physico-chemical conditions and is easily transformed into calcite by changes in the environment. Aragonite with high aspect ratios is used as a good biomedical material and filler for the improvement of mechanical properties of paper and polymer materials, because it is denser than calcite and can be integrated, resolved and replaced easily (Wang et al., 2006, Lei et al., 2006, Park et al., 2008a,b).

#### **2.4.3 *Vaterite***

Vaterite particles do not show well-defined morphologies, and usually aggregate into spherical particles or disk like shape. A definitive crystal structure of the third polymorph vaterite is not as well understood as the other polymorphs. There is a general agreement that the unit cell of vaterite is hexagonal and  $\text{CO}_3^{2-}$  ions are aligned parallel to the c-axis and not perpendicular as in the case of calcite or aragonite (Kuriyavar et al., 2000).

Vaterite is metastable whether observed in nature or prepared synthetically. This means the atoms in the crystals have a natural tendency to rearrange usually to a calcite structure. For this reason, vaterite is not commonly found in nature and is not a commercially significant form of PCC. According to Chakrabarty and Mahapatra

(1999), it is normal to form vaterite which gets transformed to the stable calcite form, when precipitation is carried out at ambient conditions especially in the presence of moisture.

In the recent years, inspired by the effect of additives, vaterite appeared in various morphologies. Among the possible additives, surfactants with charged head groups, can combine with some ions or absorb on some faces of crystals. They turned out to be very effective in controlling the morphology of inorganic materials (Ouhenia et al., 2008).

## **2.5 Nucleation and Growth**

Precipitation starts with a nucleation process (homogeneous or heterogeneous) in a supersaturated solution. Nucleation is often energetically the most difficult process in the sequence of precipitation events, because this step will start only if the energy barrier associated with the extra surface energy (change of Gibbs energy) of the clusters (nuclei) formation is overcome. Nuclei form either as spontaneous associate of growth units (molecules, ions or atoms) from the solution or by using the surface of a foreign solid phase (impurity particles) already present in the solution (heteronuclei). The dimensions of nuclei are negligible (typically less than 100 growth units) and the consumption of substance from the solution during nucleation is rather small. The nuclei formed grow into crystallites, with an occasional parallel formation of secondary nuclei initiated by the presence of the crystallizing solid phase itself). This process known as crystal growth is accompanied by the most significant changes in the solution concentration of the precipitating phase. Crystal growth itself is a complex process which may be considered to occur in two main groups of elementary processes that take

place either at some distance from the crystal surface or the crystal-solution interface (Brecevic and Krajl, 2007, Jimenez-Lopez et al., 2003).

Crystal growth and growth inhibition play an important role in the rapidly growing area of nanoscale materials. The size distribution of nanometer particles is determined by the rate of nucleation of the solid cores and the subsequent growth. For a given amount of material, the ratio between the rates of these two processes determines the size and number of the particles. The fast nucleation tends to produce smaller and more numerous particles; while the growth is the predominant, the crystallite usually is composed of larger particles. Accelerated nucleation and inhibited growth, therefore, are the key factors for the synthesis of nanometer particles in aqueous solutions (Lin et al., 2002).

Decrease in temperature, or in the flow or CO<sub>2</sub> concentration in the gas mixture, increases the number of nuclei formed, which are centres of crystallization and therefore the product contains finer particles (Vucak et al., 1997).

## **2.6 Characteristics of PCC products**

PCC is a synthetic product of mineral origin and the ability to reproducibly manufacture PCC made to a particular size, shape or other specifications is called crystal engineering. The combination of chemical synthesis and crystal engineering allows for five distinct characteristics of the product to be tailored. According to Specialty Minerals Inc. (SMI), these characteristics were called as five degrees of freedom of PCC (Specialty, 2008).