SYNTHESIS OF NANO-PRECIPITATED CALCIUM CARBONATE USING HIGH GRAVITY PACKED BED REACTOR (HGRPB)

MR. KITTISAK DAOCHANTUEK

MR. TEERAKORN WILAKUANG

MISS SIRIKARN KAMOLPIYAPAT

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Student Names	Mr. Kittisak Daochantuek Mr. Teerakorn Wilakuang Miss Sirikarn Kamolpiyapat
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Special Project Advisor	Asst. Prof. Pachernchai Chaiyasith

Abstract

This project involves synthesis of Nano-precipitated calcium carbonate (NPCC) using high gravity rotating packed bed (HGRPB). HGRPB reactor was designed, constructed and used for preparation of NPCC. Concentration of $Ca(OH)_2$ and CO_2 were investigated in this study with fixed parameters. Rotating speed of stirrer motor was at 2000 rpm. Liquid flow rate was at 9 liter/min while CO_2 pressure was fixed at 10 Pa at room-temperature. Three parts of experiment had been adapted for expected result as nanometer range. It was found that HGRPB reactor was able to prepare for NPCC of 200 nm at concentration around 2 g/l. However, NPCC was confirmed using x-ray diffraction and scanning electron microscope.

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Mr. Kittisak Daochantuek

Mr. Teerakorn Wilakuang

Miss Sirikarn Kamolpiyapat

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Chapter 1

Introduction

1.1. Rationale

Nanotechnology is the creation of new material, devices, and systems through the control of matter on the nanometer-length scale, at the level of atoms and molecules. The essence of nanotechnology is the ability to work at these levels to generate nanostructures with fundamentally new molecular organization. Finely dispersed nanostructure or nanoparticles are used in numerous technological and medical applications such as ceramic, polymer composites, filter material, pigment, electronic, catalysts and many others. Several techniques have been developed for such particles, some based on physical and some based on chemical principles. Used mechanical grinding as a means to attain particles in the nanoscale (<100 nm) is not practical for various reasons:

- The grain distribution is large.
- Obtaining particles smaller than 1um is usually difficult, and can not be controlled easily.
- The shape is irregular due to non-directed cracking.
- Particle size distribution is broad and uncontrolled.

Therefore the need for wet chemical procedure is important. Wet chemical procedures have been found to be promising due to their low energy requirements and better controller the particle size. However when nanometer sized $CaCO_3$ particle are used in the polymer-particle

interface areas, it increases drastically and steric hindrances are reduced. This can cause significant changes in the properties of the composite.

Calcium carbonate ($CaCO_3$) is a common substance found as rock in all parts of the world, and is the main component of shells of marine organisms, snails, and eggshells. Calcium carbonate is the active ingredient in agricultural lime, and is usually the principal cause of hard water. It is commonly used medicinally as a calcium supplement or as an antacid, but high consumption can be hazardous.

The vast majority of calcium carbonate used in industry is extracted by mining or quarrying. Pure calcium carbonate (e.g. for food or pharmaceutical use), can be produced from a pure quarried source (usually marble).

Calcium carbonate grades, in the form of powders, granules and slurries, are produced in 2 ways: through the extraction and processing of natural ores or synthetically through chemical precipitation. Ground calcium carbonate (GCC) is primarily based on limestone and chalk, though marble stone is imported and processed at a few locations. Precipitated Calcium Carbonate (PCC) is produced through a recarbonisation process or as a by-product of some bulk chemical processes.

Generally, normal calcium oxide is prepared by calcining crude calcium carbonate. Water is added to give calcium hydroxide, and carbon dioxide is passed through this solution to precipitate the desired calcium carbonate, referred to in the industry as precipitated calcium carbonate or call PCC.

There are various methods to produce PCC nanoparticles. For example, gas evaporation [1], however, thermal evaporation is a known limitation to this method for metals and intermetallic compounds.

Sputtering [2] is one of method enabling the synthesis of nanoparticles. However, small changes in pressure of Ar would change the particle size.

Mechanochemical synthesis [3] by placing $CaCl_2$, Na_2CO_3 and NaCl in a ball miller obtained $CaCO_3$ in a NaCl matrix. However, NaCl waste is its disadvantage.

Double water in oil emulsion method [4] or modified LEM was developed to reduce the expensive cost of synthesis equipment. However, it formed larger particles than expected.

Jianfeng Chen at Beijing University who researched high gravity method, developed the high gravity reactive precipitation (HGRP) with low cost [5] to synthesize the mass production of 15-30 nm $CaCO_3$. Although HGRP method produces expected nanoparticles, but still required expensive synthesis equipment. Therefore, simplified HGRP has been developed in this study to produce PCC nanoparticles.

High gravity method [6] has been employed for the synthesis of inorganic and organic nanoparticles via gas-liquid, liquid-liquid, and gas-liquid-solid multiphase reactions, e.g. inorganic nanoparticles like nanosized $CaCO_3$, TiO_2, SiO_2, ZnO, Al_2O_3, ZnS, $BaTiO_3$, $BaCO_3$, $SrCO_3$, $Al(OH)_3$ and $Mg(OH)_2$ flame retardants, and organic nano-pharmaceuticals including benzoic acid, salbutamol sulfate and cephradine. This technology has received extensive attention in the field of nanomaterials fabrication and application.

At nanometer length scale, new properties and new phenomena come about, materials start behaving differently. The reduced size of nanoparticles is responsible for changed electronic, optical and magnetic properties of nanoparticles and nanostructured materials in comparison with the bulk material. As a result, in the case of sealants and adhesives, PCCs nanoparticles (0.06 to 0.15 micron in size) build true thixotropic structure in sealants and adhesives when used at a 10 percent or higher loading. PCC as a rheological additive provides viscosity, thixotropy, shear thinning, and yield value for economical control of slump, sag, and extrusion or spray-application rates. The nano also reinforce the polymers, increasing tensile strength and modulus.

Nano or ultrafine calcium carbonate ($CaCO_3$) particles have a variety of applications in paper, rubber and paint manufacturing, cosmetics, as nucleating agents or fillers in polymerization, and have even been suggested for use in drug delivery.

In Thailand, currently, has 800,000 metric tons/year production capacity from approximately 10 manufacturers and 95% of the products are for domestic use. Demand of calcium carbonate is increasing as a result of 80% of the production is emphasized on hi-end calcium carbonate [7].

1.2. Objectives

- To design and construct a high gravity rotating packed bed HGRPB reactor.
- To prepare Nano-precipitated calcium carbonate (NPCC).

1.3. Scopes of study

- To design and construct the HGRPB reactor in lab scale.

- To find condition of the preparation method for NPCC by using constructed HGRPB reactor.

1.4. Expected result

- To obtain HGRPB reactor for preparing NPCC with the particle size in nanometer range.

Chapter 2

Theoretical Consideration and Literature Review

Part I. Materials

2.1. Calcium carbonate [8]

Figure 2.1: Calcium carbonate powder

Calcium carbonate is a chemical compound with the chemical formula $CaCO_3$. It is a common substance found as rock in all parts of the world. Calcium carbonate is the active ingredient in agricultural lime, and is usually the principal cause of hard water. It is commonly used medicinally as a calcium supplement or as an antacid, but high consumption can be hazardous.

2.1.1 Occurrence

Calcium carbonate occurs abundantly in several natural minerals and rocks such as

- Aragonite
- Calcite
- Vaterite or (μ-$CaCO_3$)
- Chalk (Blackboard chalk is calcium sulfate, $CaSO_4$)
- Limestone
- Marble
- Travertine

2.1.2 Limestone Resources of Thailand

There are a lot of area of limestone in Thailand i.e. Narathiwat, Suratthani, Ranong, Phangnar, Chumphon, Songkhla, Rayong,Satun, Chanthaburi, Prachuapkhirikhan, Uttaradit, Phetchabun, Chiangrai, Nakhonsawan, Lampang, Chiangmai, Suphanburi, Ayuttaya, Loei, Nakhonpathom, Phitsanulok, Khonkaen, Bangkok, Batdambang, Maehongson, Nan, Moulmein, Li, Banmi, Ye, and Vientane.

2.1.3 Chemical properties

Calcium carbonate shares the typical properties of other carbonates. Notably:

1. It reacts with strong acids, releasing carbon dioxide:

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

2. It releases carbon dioxide on heating (to above 840 °C in the case of $CaCO_3$), to form calcium oxide, commonly called quicklime, with reaction enthalpy 178 kJ / mole:

$$CaCO_3 \longrightarrow CaO + CO_2$$

Calcium carbonate will react with water that is saturated with carbon dioxide to form the soluble calcium bicarbonate.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

2.1.4 Preparation

The vast majority of calcium carbonate used in industry is extracted by mining or quarrying. Pure calcium carbonate (e.g. for food or pharmaceutical use), can be produced from a pure quarried source (usually marble).

Alternatively, calcium oxide is prepared by calcining crude calcium carbonate. Water is added to give calcium hydroxide, and carbon dioxide is passed through this solution to precipitate the desired calcium carbonate, referred to in the industry as precipitated calcium carbonate (PCC):

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

2.1.5 Solubility

2.1.5.1 With varying CO_2 pressure

Table 2.1: Calcium ion solubility as a function of CO_2 partial pressure at 25 °C

Calcium ion solubility as a function of CO_2 partial pressure at 25 °C ($K_{sp} = 4.47\times10^{-9}$)		
P_{CO_2} (atm)	pH	$[Ca^{2+}]$ (mol/L)
10^{-12}	12.0	5.19×10^{-3}
10^{-10}	11.3	1.12×10^{-3}
10^{-8}	10.7	2.55×10^{-4}
10^{-6}	9.83	1.20×10^{-4}
10^{-4}	8.62	3.16×10^{-4}
3.5×10^{-4}	**8.27**	**4.70×10^{-4}**
10^{-3}	7.96	6.62×10^{-4}
10^{-2}	7.30	1.42×10^{-3}
10^{-1}	6.63	3.05×10^{-3}
1	5.96	6.58×10^{-3}
10	5.30	1.42×10^{-2}

Calcium carbonate is poorly soluble in pure water (47 mg/L at normal atmospheric CO_2 partial pressure as shown below).

The equilibrium of its solution is given by the equation (with dissolved calcium carbonate on the right):

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad K_{sp} = 3.7\times10^{-9} \text{ to } 8.7\times10^{-9} \text{ at } 25\ ^\circ C$$

where the solubility product for $[Ca^{2+}][CO_3^{2-}]$ is given as anywhere from $K_{sp} = 3.7\times10^{-9}$ to $K_{sp} = 8.7\times10^{-9}$ at 25 °C, depending upon the data source. What the equation means is that the product of molar concentration of calcium ions (moles of dissolved Ca^{2+} per liter of solution) with the molar concentration of dissolved CO_3^{2-} cannot exceed the value of K_{sp}. This seemingly simple solubility equation, however, must be taken along with the more complicated equilibrium of carbon dioxide with water (see carbonic acid). Some of the CO_3^{2-} combines with H^+ in the solution according to:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_{a2} = 5.61\times10^{-11} \text{ at } 25\ ^\circ C$$

HCO_3^- is known as the bicarbonate ion. Calcium bicarbonate is many times more soluble in water than calcium carbonate -- indeed it exists only in solution.

Some of the HCO_3^- combines with H^+ in solution according to:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_{a1} = 2.5\times10^{-4} \text{ at } 25\ ^\circ C$$

Some of the H_2CO_3 breaks up into water and dissolved carbon dioxide according to:

$$H_2O + CO_2(\text{dissolved}) \rightleftharpoons H_2CO_3 \qquad K_h = 1.70\times10^{-3} \text{ at } 25\ ^\circ C$$

And dissolved carbon dioxide is in equilibrium with atmospheric carbon dioxide according to:

$$\frac{P_{CO_2}}{[CO_2]} = k_H$$

where $k_H = 29.76$ atm/(mol/L) at 25 °C (Henry constant), P_{CO_2} being the CO_2 partial pressure.

For ambient air, P_{CO2} is around 3.5×10^{-4} atmospheres (or equivalently 35 Pa). The last equation above fixes the concentration of dissolved CO_2 as a function of P_{CO2}, independent of the concentration of dissolved $CaCO_3$. At atmospheric partial pressure of CO_2, dissolved CO_2

concentration is 1.2×10^{-5} moles/liter. The equation before that fixes the concentration of H_2CO_3 as a function of $[CO_2]$. For $[CO_2]=1.2\times10^{-5}$, it results in $[H_2CO_3]=2.0\times10^{-8}$ moles per liter. When $[H_2CO_3]$ is known, the remaining three equations together with

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K = 10^{-14} \text{ at } 25\ ^\circ C$$

(which is true for all aqueous solutions), and the fact that the solution must be electrically neutral,

$$2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

make it possible to solve simultaneously for the remaining five unknown concentrations (note that the above form of the neutrality equation is valid only if calcium carbonate has been put in contact with pure water or with a neutral pH solution; in the case where the origin water solvent pH is not neutral, the equation is modified).

The table 2.1 shows the result for $[Ca^{2+}]$ and $[H^+]$ (in the form of pH) as a function of ambient partial pressure of CO_2 ($K_{sp} = 4.47\times10^{-9}$ has been taken for the calculation).

1. At atmospheric levels of ambient CO_2 the table indicates the solution will be slightly alkaline with a maximum $CaCO_3$ solubility of 47 mg/L.

2. As ambient CO_2 partial pressure is reduced below atmospheric levels, the solution becomes more and more alkaline. At extremely low P_{CO_2}, dissolved CO_2, bicarbonate ion, and carbonate ion largely evaporate from the solution, leaving a highly alkaline solution of calcium hydroxide, which is more soluble than $CaCO_3$. Note that for $P_{CO_2}=10^{-12}$ atm, the $[Ca^{2+}][OH^-]^2$ product is still below the solubility product of $Ca(OH)_2$ (8×10^{-6}). For still lower CO_2 pressure, $Ca(OH)_2$ precipitation will occur before $CaCO_3$ precipitation.

3) As ambient CO_2 partial pressure increases to levels above atmospheric, pH drops, and much of the carbonate ion is converted to bicarbonate ion, which results in higher solubility of Ca^{2+}.

The effect of the latter is especially evident in day to day life of people who have hard water. Water in aquifers underground can be exposed to levels of CO_2 much higher than atmospheric. As such water percolates through calcium carbonate rock, the $CaCO_3$ dissolves according to the second trend. When that same water then emerges from the tap, in time it comes into equilibrium with CO_2 levels in the air by outgassing its excess CO_2. The calcium carbonate becomes less soluble as a result and the excess precipitates as lime scale. This same process is responsible for the formation of stalactites and stalagmites in limestone caves.

Two hydrated phases of calcium carbonate, monohydrocalcite, $CaCO_3 \cdot H_2O$ and ikaite, $CaCO_3 \cdot 6H_2O$, may precipitate from water at ambient conditions and persist as metastable phases.

2.1.5.2 With varying pH

We now consider the problem of the maximum solubility of calcium carbonate in normal atmospheric conditions ($P_{CO_2} = 3.5 \times 10^{-4}$ atm) when the pH of the solution is adjusted. This is for example the case in a swimming pool where the pH is maintained between 7 and 8 (by addition of sodium bisulfate $NaHSO_4$ to decrease the pH or of sodium bicarbonate $NaHCO_3$ to increase it). From the above equations for the solubility product, the hydratation reaction and the two acid reactions, the following expression for the maximum $[Ca^{2+}]$ can be easily deduced:

$$[Ca^{2+}]_{max} = \frac{K_{sp} k_H}{K_h K_{a1} K_{a2}} \frac{[H^+]^2}{P_{CO_2}}$$

showing a quadratic dependence in $[H^+]$. The numerical application with the above values of the constants gives

Table 2.2: The maximum solubility of calcium carbonate when the pH of the solution is adjusted.

pH	7.0	7.2	7.4	7.6	7.8	8.0	8.2	8.27	8.4
$[Ca^{2+}]_{max}$ (10^{-4} mol/L or °f)	1590	635	253	101	40.0	15.9	6.35	4.70	2.53
$[Ca^{2+}]_{max}$ (mg/L)	6390	2540	1010	403	160	63.9	25.4	18.9	10.1

Comments:

- decreasing the pH from 8 to 7 increases the maximum Ca^{2+} concentration by a factor 100. Water with a pH maintained to 7 can dissolve up to 15.9 g/L of $CaCO_3$. This explains the high Ca^{2+} concentration in some mineral waters with pH close to 7.
- note that the Ca^{2+} concentration of the previous table is recovered for pH = 8.27.
- keeping the pH to 7.4 in a swimming pool (which gives optimum $HClO/ClO^-$ ratio in the case of "chlorine" maintenance) results in a maximum Ca^{2+} concentration of 1010 mg/L. This means that successive cycles of water evaporation and partial renewing may result in a very hard water before $CaCO_3$ precipitates (water with a Ca^{2+} concentration above 120 mg/L or 30 °f is considered very hard). Addition of a calcium sequestring agent or complete renewing of the water will solve the problem.

2.1.5.3 Solubility in a strong or weak acid solution

Solutions of strong (HCl) or weak (acetic, sorbic, lactic, phosphoric) acids are commercially available. They are commonly used as descaling agents to remove limescale deposits. The maximum amount of $CaCO_3$ that can be "dissolved" by one liter of an acid solution can be calculated using the above equilibrium equations.

- In the case of a strong monoacid with decreasing acid concentration $[A] = [A^-]$, we obtain (with $CaCO_3$ molar mass = 100 g):

Table 2.3: Solubility of $CaCO_3$ in the case of strong monoacid

[A] (mol/L)	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-10}
Initial pH	0.00	1.00	2.00	3.00	4.00	5.00	6.00	6.79	7.00
Final pH	6.75	7.25	7.75	8.14	8.25	8.26	8.26	8.26	8.27
Dissolved $CaCO_3$ (g per liter of acid)	50.0	5.00	0.514	0.0849	0.0504	0.0474	0.0471	0.0470	0.0470

where the initial state is the acid solution with no Ca^{2+} (not taking into account possible CO_2 dissolution) and the final state is the solution with saturated Ca^{2+}. For strong acid concentrations, all species have a negligible concentration in the final state with respect to Ca^{2+} and A^- so that the neutrality equation reduces approximately to $2[Ca^{2+}] = [A^-]$ yielding $[Ca^{2+}] \simeq \frac{[A^-]}{2}$. When the concentration decreases, $[HCO_3^-]$ becomes non negligible so that the preceding expression is no longer valid. For vanishing acid concentrations, we recover the final pH and the solubility of $CaCO_3$ in pure water.

- In the case of a weak monoacid (here we take acetic acid with $pK_A = 4.76$) with decreasing total acid concentration $[A] = [A^-]+[AH]$, we obtain:

Table 2.4: Solubility of $CaCO_3$ in the case of weak monoacid

[A] (mol/L)	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-10}
Initial pH	2.38	2.88	3.39	3.91	4.47	5.15	6.02	6.79	7.00
Final pH	6.75	7.25	7.75	8.14	8.25	8.26	8.26	8.26	8.27
Dissolved $CaCO_3$ (g per liter of acid)	49.5	4.99	0.513	0.0848	0.0504	0.0474	0.0471	0.0470	0.0470

See that for the same total acid concentration, the initial pH of the weak acid is less acid than the one of the strong acid; however, the maximum amount of $CaCO_3$ which can be dissolved is approximately the same. This is because in the final state, the pH is larger that the pKA, so that

the weak acid is almost completely dissociated, yielding in the end as many H+ ions as the strong acid to "dissolve" the calcium carbonate

- The calculation in the case of phosphoric acid (which is the most widely used for domestic applications) is more complicated since the concentrations of the four dissociation states corresponding to this acid must be calculated together with $[HCO^{3-}]$, $[CO_3^{2-}]$, $[Ca^{2+}]$, $[H^+]$ and $[OH^-]$. The system may be reduced to a seventh degree equation for [H+] the numerical solution of which gives

Table 2.5: Solubility of $CaCO_3$ in the case of phosphoric acid

[A] (mol/L)	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-10}
Initial pH	1.08	1.62	2.25	3.05	4.01	5.00	5.97	6.74	7.00
Final pH	6.71	7.17	7.63	8.06	8.24	8.26	8.26	8.26	8.27
Dissolved $CaCO_3$ (g per liter of acid)	62.0	7.39	0.874	0.123	0.0536	0.0477	0.0471	0.0471	0.0470

where $[A] = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$ is the total acid concentration. We see that phosphoric acid is more efficient than a monoacid since at the final almost neutral pH, the second dissociated state concentration $[HPO_4^{2-}]$ is not negligible (see phosphoric acid).

2.1.6 Uses

2.1.6.1 Industrial applications

The main use of calcium carbonate is in the construction industry, either as a building material in its own right (e.g. marble) or limestone aggregate for road-building or as an ingredient of cement or as the starting material for the preparation of builder's lime by burning in a kiln.

Calcium carbonate is also used in the purification of iron from iron ore in a blast furnace. Calcium carbonate is calcined in situ to give calcium oxide, which forms a slag with various impurities present, and separates from the purified iron.

Calcium carbonate is also used in the oil industry in drilling fluids as a formation bridging and filtercake sealing agent and may also be used as a weighting material to increase the density of drilling fluids to control downhole pressures.

Calcium carbonate is also one of the main sources used in growing Seacrete, or Biorock.

Calcium carbonate is widely used as an extender in paints, in particular matte emulsion paint where typically 30% by weight of the paint is either chalk or marble.

Calcium carbonate is also widely used as a filler in plastics. Some typical examples include around 15 to 20% loading of chalk in uPVC drain pipe, 5 to 15% loading of stearate coated chalk or marble in uPVC window profile. PVC cables can use calcium carbonate at loadings of up to 70 phr (parts per hundred parts of resin) to improve mechanical properties (tensile strength and elongation) and electrical properties (volume resistivity). Polypropylene compounds are often filled with calcium carbonate to increase rigidity, a requirement that becomes important at high use temperatures. It also routinely used as a filler in thermosetting resins (Sheet and Bulk moulding compounds) and has also been mixed with ABS, and other ingredients, to form some types of compression molded "clay" Poker chips.

Fine ground calcium carbonate is an essential ingredient in the microporous film used in babies' diapers and some building films as the pores are nucleated around the calcium carbonate particles during the manufacture of the film by biaxial stretching.

Calcium carbonate is also used in a wide range of trade and DIY adhesives, sealants, and decorating fillers. Ceramic tile adhesives typically contain 70 to 80% limestone. Decorating crack

fillers contain similar levels of marble or dolomite. It is also mixed with putty in setting stained glass windows, and as a resist to prevent glass from sticking to kiln shelves when firing glazes and paints at high temperature.

Calcium carbonate is known as whiting in ceramics/glazing applications, where it is used as a common ingredient for many glazes in its white powdered form. When a glaze containing this material is fired in a kiln, the whiting acts as a flux material in the glaze.

In North America, calcium carbonate has begun to replace kaolin in the production of glossy paper. Europe has been practicing this as alkaline papermaking or acid-free papermaking for some decades. Carbonates are available in forms: ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC). The latter has a very fine and controlled particle size, on the order of 2 micrometres in diameter, useful in coatings for paper.

It is used in swimming pools as a pH corrector for maintaining alkalinity "buffer" to offset the acidic properties of the disinfectant agent.

It is commonly called chalk as it has been a major component of blackboard chalk. Chalk may consist of either calcium carbonate or gypsum, hydrated calcium sulfate $CaSO_4 \cdot 2H_2O$.

2.1.6.2 Health and dietary applications

Calcium carbonate is widely used medicinally as an inexpensive dietary calcium supplement or antacid. It may be used as a phosphate binder for the treatment of hyperphosphatemia (primarily in patients with chronic renal failure). It is also used in the pharmaceutical industry as an inert filler for tablets and other pharmaceuticals. Calcium carbonate is also used in homeopathy as one of the constitutional remedies.

Excess calcium from supplements, fortified food and high-calcium diets, can cause the "milk alkali syndrome," which has serious toxicity and can be fatal. In 1915, Bertram Sippy introduced the "Sippy regimen" of hourly ingestion of milk and cream, and the gradual addition of eggs and cooked cereal, for 10 days, combined with alkaline powders, which provided symptomatic relief for peptic ulcer disease. Over the next several decades, the Sippy regimen resulted in renal failure, alkalosis, and hypercalemia, mostly in men with peptic ulcer disease. These adverse effects were reversed when the regimen stopped, but it was fatal in some patients with protracted vomiting. Milk alkali syndrome declined in men after effective treatments for peptic ulcer disease. But during the past 15 years, it has been reported in women taking calcium supplements above the recommended range of 1200 to 1500 mg daily, for prevention and treatment of osteoporosis, and is exacerbated by dehydration. Calcium has been added to over-the-counter products, which contributes to inadvertent excessive intake. Excessive calcium intake can lead to hypercalcemia, complications of which include vomiting, abdominal pain and altered mental status.

A form of food additive is designated as E170. It is used in some soy milk products as a source of dietary calcium; one study suggests that calcium carbonate might be bioavailable as the calcium in cow's milk.

2.1.6.3 Ecological applications

In 1989, a researcher, Ken Simmons, introduced $CaCO_3$ into the Whetstone Brook in Massachusetts. His hope was that the calcium carbonate would counter the acid in the stream from acid rain and save the trout that had ceased to spawn. Although his experiment was a success, it did increase the amounts of aluminium ions in the area of the brook that was not treated with the limestone. This shows that $CaCO_3$ can be added to neutralize the effects of acid

rain in river ecosystems. Currently calcium carbonate is used to neutralize acidic conditions in both soil and water.

2.2. Calcium oxide [9]

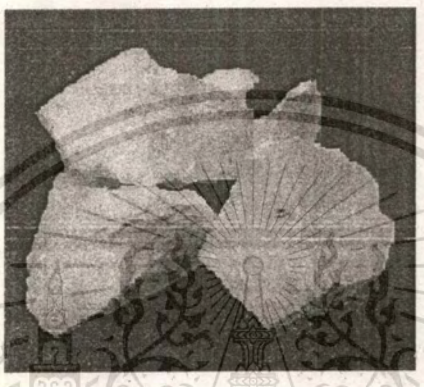


Figure 2.2: Calcium oxide

- **Other names:** Quicklime
- **Molecular formula:** CaO
- **Molar mass:** 56.077 g/mol
- **Appearance:** White to pale yellow powder
- **Density:** 3.35 g/cm^3
- **Melting point:** 2572 °C (2845 K)
- **Boiling point:** 2850 °C (3123 K)
- **pH:** 12.5 Saturated solution in water
- **Solubility:** Reacts with water to form calcium hydroxide; soluble in acids; insoluble in alcohol and most organic solvents.
- **Solubility in water:** 1850 mg/l at 0°C
  1650 mg/l at 20°C

770 mg/l at 100°C

Calcium oxide is a white crystalline solid with a melting point of 2572°C. It is manufactured by heating limestone, coral, sea shells, or chalk, which are mainly $CaCO_3$, to drive off carbon dioxide.

$$CaCO_3(s) \xrightarrow{500\text{–}600^\circ C} CaO(s) + CO_2(g)$$

This reaction is reversible; calcium oxide will react with carbon dioxide to form calcium carbonate. The reaction is driven to the right by flushing carbon dioxide from the mixture as it is released.

The production of calcium oxide from limestone is one of the oldest chemical transformations produced by man. Its use predates recorded history. Most ancient languages have a word for calcium oxide. In Latin it is calx, from which the name of the element calcium is taken. In Old English, its name is lim, which is the origin of the modern commercial name for calcium oxide, namely lime. The abundance of limestone in the Earth's crust and the ease of its transformation to calcium oxide do not alone explain why the lime is one of the oldest products of chemistry. Lime has many properties that make it quite valuable. It is so useful, that it is today produced industrially on a vast scale; over 20 million metric tons were produced in the U.S. in 2000.

The oldest uses of lime exploit its ability to react with carbon dioxide to regenerate calcium carbonate. When lime is mixed with water and sand, the result is mortar, which is used in construction to secure bricks, blocks, and stones together. Mortar is initially a stiff paste that is laid between the bricks. It gradually hardens, cementing the bricks together. At room temperature,

the reaction of lime with carbon dioxide is very slow. It is speeded by mixing lime with water. When lime is mixed with water, it forms calcium hydroxide, called slaked lime.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

The reaction of calcium hydroxide with carbon dioxide is faster, producing a mortar that hardens more quickly.

$$Ca(OH)_2(s) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$

Even with the increased reaction speed, mortar requires many years for complete reaction to occur. Other lime & endash; based products used in the construction industry include lime plaster and portland cement.

Perhaps the most commercially important property of lime is its ability to form solutions with silicates. When lime is heated with silica sand (SiO_2) and sodium carbonate (Na_2CO_3), a solution is formed that does not crystallize when it is cooled. Instead it hardens to an amorphous, clear, and nearly colorless solid, namely glass. Because it is a mixture and not a pure compound, glass does not have a distinct melting point; it gradually softens as it is heated. Therefore, it can be molded and blown into many useful shapes. The production of glass from lime is another of the ancient uses of lime.

The most important modern use of lime also relies on its ability to form solutions with silicates. Nearly 45% of lime is used in the steel industry. Steel and iron are produced from ores, which are rocks that contain iron oxides. Many of these ores also contain a large amount of silicates. When lime is mixed with the ore and the mixture melted, these silicates combine with the lime, forming a liquid solution called slag. Slag is immiscible with molten iron, so the silicates can be removed from the iron by draining o the slag. Approximately 80 kg of lime is

used in the production of each metric ton (1000 kg) of iron. Lime is also used in the production of other metals. For example, it is used to remove silicates from alumina (Al_2O_3) before the alumina is reduced to aluminum metal.

Lime is also an important material in the manufacture of chemicals. Its major use here is in the production of calcium carbide, CaC_2. Calcium carbide is manufactured by heating lime with coke.

$$2\ CaO(s) + 5\ C(s) \longrightarrow 2\ CaC_2(s) + CO_2(g)$$

Calcium carbide reacts with water, releasing acetylene, C_2H_2.

$$CaC_2(s) + 2\ H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

Acetylene is an important fuel for welding and is also a starting material for a range of organic compounds, including vinyl chloride, neoprene, and acrylonitrile, all of which are raw materials for polymers.

Pollution control is a rapidly expanding consumer of lime. Lime is used in stack gas scrubbers to reduce sulfur dioxide emissions from power plants. Sulfur dioxide reacts with lime to form solid calcium sulfite.

$$SO_2(g) + CaO(s) \longrightarrow CaSO_3(s)$$

Lime is also added to sewage to remove phosphates.

$$3\ CaO(s) + 3\ H_2O(l) + 2\ PO_4^{3-}(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6\ OH^-(aq)$$

The pretreatment of water supplies involves the use lime to decrease the acidity, to soften, and to clear drinking water.

A variety of other industrial processes also make extensive use of lime. It is used as an opacifier in plastics. The paper industry uses it in pulping wood; because lime is highly alkaline, it dissolves the lignin that binds the fibers together in wood. In the refining of sugar, lime causes coagulation of plant material, allowing it to be more easily separated from the sugar syrup.

Calcium oxide no longer produces the limelight in theaters. The theatrical use of lime has disappeared, leaving only its name, suggesting the romance of a bygone era. Because lime has a very high melting point, it can be heated to a very high temperature without melting. Substances with such high melting points can be heated to white heat, a temperature so high that the light they emit is white. Before the advent of electric lighting, white stage lighting was produced by heating lime in the flame of a torch, and this light was called limelight.

2.3. Calcium hydroxide [10]

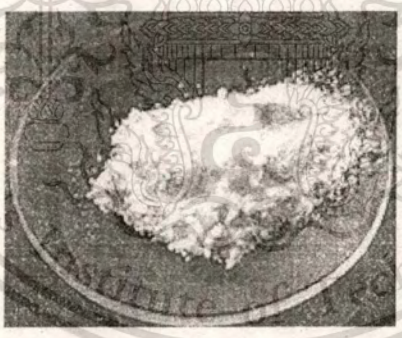


Figure 2.3: Calcium hydroxide powder

- **Other names:** Slaked lime, Milk of lime, Calcium(II) hydroxide, Pickling lime
- **Molecular formula:** $Ca(OH)_2$
- **Molar mass:** 74.09 g/mol
- **Appearance:** Soft white powder/Colourless liquid

- **Density:** 2.211 g/cm^3, solid Density 2.211 g/cm^3, solid
- **Melting point:** 512 °C (decomp.)
- **Solubility in water:** 0.185 g/100 cm^3 , K_{sp} = 7.9×10^{-6}\
- **Basicity:** (pK_b) 2.37
- **Related compounds:** Other cations Magnesium hydroxide,

  Strontium hydroxide, Barium hydroxide
- **Related bases:** Calcium oxide

Calcium hydroxide is a chemical compound with the chemical formula $Ca(OH)_2$. It is a colourless crystal or white powder, and is obtained when calcium oxide (called lime or quicklime) is mixed, or "slaked" with water. It can also be precipitated by mixing an aqueous solution of calcium chloride and an aqueous solution of sodium hydroxide. The name of the natural, mineral form is portlandite. It is relatively rare mineral, known from some volcanic, plutonic and metamorphic rocks. Sometimes it arises on burning coal dumps, too.

When heated to 512 °C, the partial pressure of water in equilibrium with calcium hydroxide reaches 101 kPa and decomposes into calcium oxide and water. A suspension of fine calcium hydroxide particles in water is called milk of lime. The solution is called lime water and is a medium strength base that reacts violently with acids and attacks many metals in presence of water. It turns milky if carbon dioxide is passed through, due to precipitation of calcium carbonate.

2.3.1 Uses

Because of its strong basic properties, calcium hydroxide has many and varied uses:

- A flocculant, in water and sewage treatment and improvement of acid soils
- An ingredient in whitewash, mortar, and plaster

- An alkali used as a lye substitute in no-lye hair relaxers
- A chemical depilatory agent found in Nair
- An ingredient in baby formula milk
- A chemical reagent
    - In the reef aquarium hobby for adding bio-available calcium in solution for calcium-using animals such as algae, snails, hard tube worms, and Corals (often referred to as Kalkwasser mix), and also to increase the alkalinity of the water.
    - In the tanning industry for neutralization of acid, the liming of hides and skins and the flocculation of wastewater.
    - In the petroleum refining industry for the manufacture of additives to oils (salicatic, sulphatic, fenatic)
    - In the chemical industry for manufacture of calcium stearate
    - In the food industry for processing water (for alcoholic and soft drinks)
    - For clearing a brine of carbonates of calcium and magnesium in the manufacture of salt for food and pharmacopoeia
    - In Native American and Latin American cooking, calcium hydroxide is called "cal". Corn cooked with cal becomes nixtamal which significantly increases its nutrition value, and is also considered tastier and easier to digest.
    - In chewing Betel nut or coca leaves, calcium hydroxide is usually chewed alongside to keep the alkaloid stimulants chemically available for absorption by the body
    - Similarly, Native Americans traditionally chewed tobacco leaves with calcium hydroxide derived from burnt shells to enhance the effects
- A filler
    - In the petrochemical industry for manufacturing solid oil of various marks
    - In the manufacture of brake pads

- In the manufacture of ebonite
- For preparation of dry mixes for painting and decorating
- In manufacturing mixes for pesticides
- In manufacturing the trademarked compound "Polikar", an antifungal and antimicrobial preservative for vegetables in storage

- In Dentistry, it is used as dressing in paste form used for anti-microbial effect during a dental root canal procedure. Calcium hydroxide is known to have a strong anti-microbial effect and is a bone-regeneration stimulant.
- It has been proposed to add it to sea water in great quantities to reduce atmospheric CO2 and fight the greenhouse effect.
  - Used as an acid suppressor in the production of metals. Lime is injected into the waste gas stream to neutralise acids such as fluorides and chlorides prior to being released to atmosphere.

2.4. Carbon dioxide [11]

Carbon dioxide, CO_2, is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm. Commercially, CO_2 finds uses as a refrigerant (dry ice is solid CO_2), in beverage carbonation, and in fire extinguishers. Because the concentration of carbon dioxide in the atmosphere is low, it is not practical to obtain the gas by extracting it from air. Most commercial carbon dioxide is recovered as a by-product of other processes, such as the production of ethanol by fermentation and the manufacture of ammonia. Some CO_2 is obtained from the combustion of coke or other carbon-containing fuels.

$$C(coke) + O_2\,(g) \longrightarrow CO_2\,(g)$$

Carbon dioxide is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO_2 in the atmosphere has increased over the past century, now rising at a rate of about 1 ppm per year. Major changes in global climate could result from a continued increase in CO_2 concentration.

In addition to being a component of the atmosphere, carbon dioxide also dissolves in the water of the oceans. At room temperature, the solubility of carbon dioxide is about 90 cm3 of CO_2 per 100 mL of water. In aqueous solution, carbon dioxide exists in many forms. First, it simply dissolves.

$$CO_2\,(g) \longrightarrow CO_2\,(aq)$$

Then, an equilibrium is established between the dissolved CO_2 and H_2CO_3, carbonic acid

$$CO_2\,(aq) + H_2O(l) \rightleftharpoons H_2CC_3\,(aq)$$

Only about 1% of the dissolved CO2 exists as $H2CO_3$. Carbonic acid is a weak acid which dissociates in two steps.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad K_{a1} = 4.2 \times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad K_{a2} = 4.8 \times 10^{-11}$$

As carbon dioxide dissolves in sea water, an equilibrium is established involving the carbonate ion, CO_3^{2-}. The carbonate anion interacts with cations in seawater. According to the solubility rules, "all carbonates are insoluble except those of ammonium and Group IA elements."

Therefore, the carbonate ions cause the precipitation of certain ions. For example, Ca^{2+} and Mg^{2+} ions precipitate from large bodies of water as carbonates. For $CaCO_3$, the value of Ksp is 5×10^{-9}, and for $MgCO_3$, Ksp is 2×10^{-3}. Extensive deposits of limestone ($CaCO_3$) and dolomite (mixed $CaCO_3$ and $MgCO_3$) have been formed in this way. Calcium carbonate is also the main constituent of marble, chalk, pearls, coral reefs, and clam shells. Although "insoluble" in water, calcium carbonate dissolves in acidic solutions. The carbonate ion behaves as a Brønsted base.

$$CaCO_3\,(s) + 2\,H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2CO_3\,(aq)$$

The aqueous carbonic acid dissociates, producing carbon dioxide gas.

$$H_2CO_3\,(aq) \longrightarrow H_2O(l) + CO_2\,(g)$$

In nature, surface water often becomes acidic because atmospheric CO2 dissolves in it. This acidic water can dissolve limestone:

$$CO_2\,(aq) + H_2O(l) + CaCO_3\,(s) \longrightarrow Ca^{2+}(aq) + 2\,HCO_3^-(aq)$$

This reaction occurs in three steps.

$$CaCO_3\,(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3\,(aq)$$

$$H_2CO_3\,(aq) + CO_3^{2-}(aq) \rightleftharpoons 2\,HCO_3^-(aq)$$

In the third step, carbonate ions accept hydrogen ions from carbonic acid. This reaction often occurs underground when rainwater saturated with CO_2 seeps through a layer of limestone.

As the water dissolves calcium carbonate, it forms openings in the limestone. Caves from which the limestone has been dissolved are often prevalent in areas where there are large deposits of $CaCO_3$ (e.g., Mammoth Cave, Carlsbad Caverns, and Cave of the Mounds). If the water containing dissolved $Ca(HCO_3)_2$ reaches the ceiling of a cavern, the water will evaporate. As it evaporates, carbon dioxide escapes, and calcium carbonate deposit on the ceiling.

$$Ca^{2}(aq) + 2HCO_3^{-}(aq) \longrightarrow H_2O(g) + CO_2(g) + CaCO_3(s)$$

Recently, some commercial dry cleaners have begun replacing the dry cleaning solvent perchloroethylene, $Cl_2C{=}CCl_2$, with liquid CO_2. Perchloroethylene is a possible carcinogen, and has been linked to bladder, esophogeal, and other cancers. Carbon dioxide does not exist in liquid form at atmospheric pressure at any temperature. The pressure-temperature phase diagram of CO_2 shows that liquid carbon dioxide at 20EC requires a pressure of 30 atmospheres. The lowest pressure at which liquid CO_2 exists is at the triple point, namely 5.11 atm at –56.6EC.

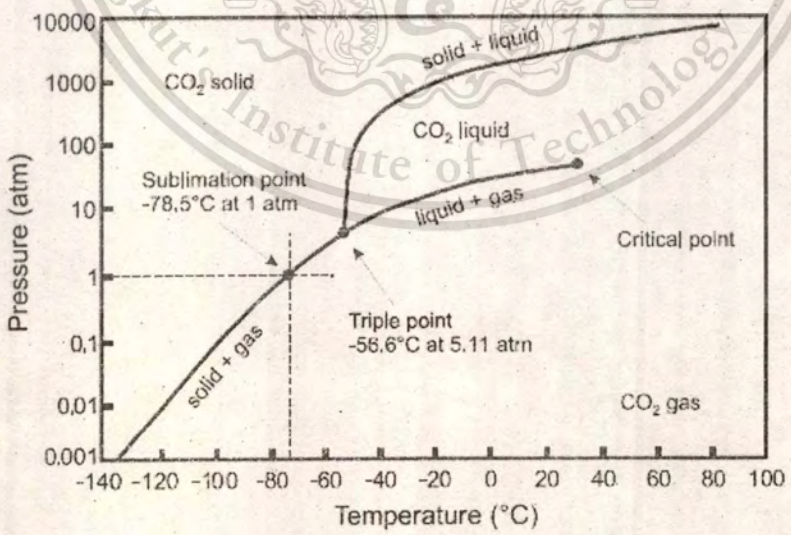


Figure 2.4: Carbon dioxide pressure-temperature phase diagram

2.5. Ground Calcium Carbonate (GCC) or Limestone [12]

Limestone is a common sedimentary rock composed primarily of the calcium carbonate mineral, calcite ($CaCO_3$). Limestone constitutes approximately 10 percent of the sedimentary rocks exposed on the earth's surface.

Limestone is formed either by direct crystallization from water (usually seawater), or by the accumulation of sea animal shells and shell fragments. In the direct crystallization case calcium ions in the seawater combine with atmospheric or dissolved carbon dioxide to form calcium carbonate, which being insoluble, precipitates out. Over time, layers of the calcium carbonate form, and with sufficient time and pressure from overlying materials, are transformed to solid rock. The chemical composition of seawater and its minerals contaminants will be recorded in the limestone impurities. Limestone frequently also contains the minerals dolomite or calcium magnesium carbonate ($CaMg(CO_3)_2$, and a second crystalline form of calcium carbonate, aragonite.

In the seas that covered much of the earth in earlier geological times lived many clams and other shelled forms of animal life. When the animals died, their shells, which are composed of calcium carbonate, fell to the bottom. Thick layers, which can be a mile or 2 kilometers deep, gradually were changed into rock. If the shells were only compressed, with little crystallization occurring, soft chalk results. The White Cliffs of Dover in England are made of this type of chalk. With more time and pressure, a coarsely crystallized rock can form, which is limestone. In limestone, most traces of the animal shells have disappeared.

Pure calcite, dolomite, and aragonite which are in the limestones, are clear or white. However, with impurities, they can take on a variety of colors, commonly white, tan or gray. Limestone can also have gone through metamorphosis, with high pressure, heat and time creating marble. This process tends to intensify the color of the stone as well as changing the nature of

some of the impurities. Metamorphosis creates the beautiful marbles seen in architectural applications.

2.5.1 Uses For Limestone

Limestone and marble are important building materials in most parts of the world. They are used as cut dimension stone (blocks and slabs) for building. In the form of coarsely crushed stone or aggregate limestone is used for general building purposes, roadbeds and as a component in concrete. When heated, the calcium carbonate in limestone decomposes to lime, or calcium oxide, which also has many industrial applications, including the manufacture of precipitated calcium carbonate (PCC). Either limestone or marble may be used as the basis for crushed or ground calcium carbonate. Ground calcium carbonate, commonly referred to as GCC is very widely used as an industrial mineral. Three primary attributes: particle size, color and chemical purity define the quality of the GCC, and define the suitability of use for any given application.

Ground limestones are available in a broad range of sizes. When specifying the size of a ground calcium carbonate, either the top size (the size of the largest particles) or the median particle size (essentially the average) can be used. Commercially, top size is generally specified for coarser industrial minerals which may be as big as beach sand, which is 10 mesh or 2 millimeters or approximately 0.1 inch in size, or as fine as flour; which is 200 mesh, or 75 microns. Finely ground calcium carbonates can range down in particle size to just a few microns, 1 to 3, with the top size controlled for high performance applications to as fine as 5 to 10 microns.

Limestone color can range from brilliant white to light gray and chemical purity can range from only 80-90% calcium carbonate to well over 99.9% purity.

Calcium carbonate is not a particularly hard mineral, with pure calcite falling at about 3 on the Mohs scale of 1 (talc) to 10 (diamond). Silica impurities in the limestone can raise the hardness of some ground calcium carbonates to a Mohs value of 4. Calcium carbonate is subject to attack by acidic environments, which has led to the damage of limestone buildings and monuments by acid rain. For industrial uses, the effect of an acid can be somewhat reduced by treating the ground limestone powder with fatty acids to put a non-polar, organic material on the surface. Few industrial minerals can match GCC for its combination of properties and cost.

2.6. Precipitated Calcium Carbonate (PCC)

Precipitated calcium carbonate (PCC) is available in numerous crystal morphologies and sizes, which can be tailored to optimize performance in a specific application. The product of a controlled synthesis that produces a desired morphology and particle size is called precipitated calcium carbonate or PCC. PCC improves paper bulk, brightness, light scattering, fibre coverage and printability. The most important crystalline forms of PCC are Rhombohedral calcite type, Scalenohedral calcite type and Orthorhombic acicular aragonite type (Needle-like) [13].

There are several various types of PCC grades, but the purity of PCC is usually over 99% with density of 2700 kg/m3.

PCC has a higher purity than natural or ground calcium carbonate (GCC) since impurities are removed in the production process. In chemical composition, they are the same. PCC's shape and size are different from that of ground calcium carbonate (GCC). Under high magnification, GCC is seen to be irregularly rhombohedral in shape. The PCC crystal shape depends on the product, and the particles are more uniform and regular [14].

The distribution of particle sizes in a GCC is much broader than for a PCC of the same size—that is, there are many more large particles and many more small particles than in a PCC,

and the size of the largest of the particles (the "top size") is much greater for a GCC than for a PCC. The lower top size of a PCC gives better impact resistance in plastics than with a GCC. The narrower particle size distribution allows the generation of high oil absorptions, useful in certain applications.

These differences can be seen in these photos of a PCC and a GCC of the same median particle size, 0.7 microns.

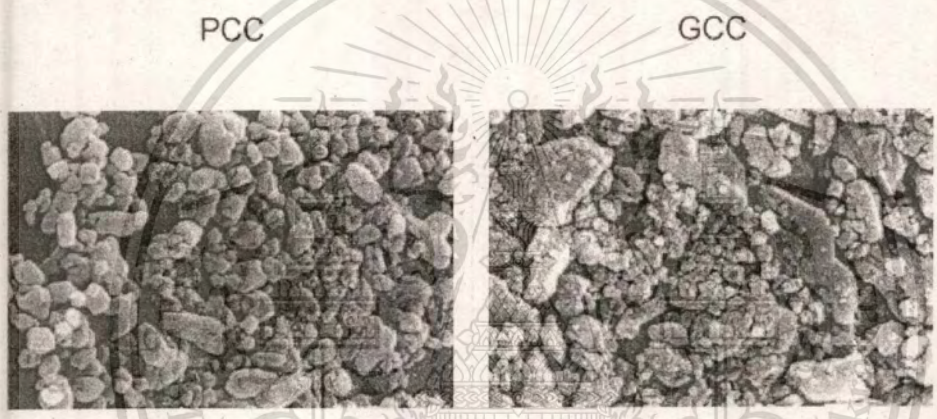


Figure 2.5: Comparison of PCC and GCC

2.6.1 Precipitated Calcium Carbonate (PCC) Chemical & Physical Properties *[15]*

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. All these polymorphs are observed in nature, and all can be produced from processes that yield synthetic precipitated calcium carbonate, or PCC. It is the arrangement of the atoms and ions in the crystal structure of these polymorphs that determine the actual physical shape of the crystal. We call these shapes morphologies, and a single polymorph, such as calcite, can exhibit several different morphologies.

The vaterite polymorph of calcium carbonate often exhibits nearly perfect spherical shapes. Even at high magnifications under an electron microscope, these spheres may appear smooth, but can be quite porous, as evidenced by techniques such as mercury porosimetry. Vaterite may also exhibit a platy structure, and when this happens, the plates tend to self-assemble into larger structures that may be spheroidal or some other shape. Whether observed in nature or prepared synthetically, vaterite is metastable. This means the atoms in the crystals have a natural tendency to rearrange usually to a calcite structure, as discussed below. For this reason, vaterite is not commonly found in nature and is not a commercially significant form of PCC.

Figure 2.6: SEM image of vaterite (spherical shape)

The aragonite polymorph generally exhibits needle-shaped orthorhombic crystals. 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. 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. These aragonite clusters behave similarly to the scalenohedral clusters discussed below.

Figure 2.7: SEM image of aragonite (needle-shaped orthorhombic)

Calcite is the most common polymorph of calcium carbonate and the most stable. Calcite is produced in rhombohedral (cubic), prismatic (barrel-shaped) and scalenohedral (triangular) morphologies. The rhombohedral and prismatic forms are useful in paper coating applications and as strength enhancers in polymer matrixes. In filled papers, large prismatic morphologies are useful for improving drainage on the paper machine and providing a bulky finished product. When applied in pigmented size applications, large prismatic PCC can help lower gloss or sheen of the paper surface.

Scalenohedral calcite can be a collection of discrete particles or a cluster of individual crystals arranged in a rosette or starbust pattern. The latter morphology is commonly used in paper filling because this unique shape scatters light efficiently, which significantly enhances paper opacity. Large scalenohedral particles also increase bulk in filled papers.

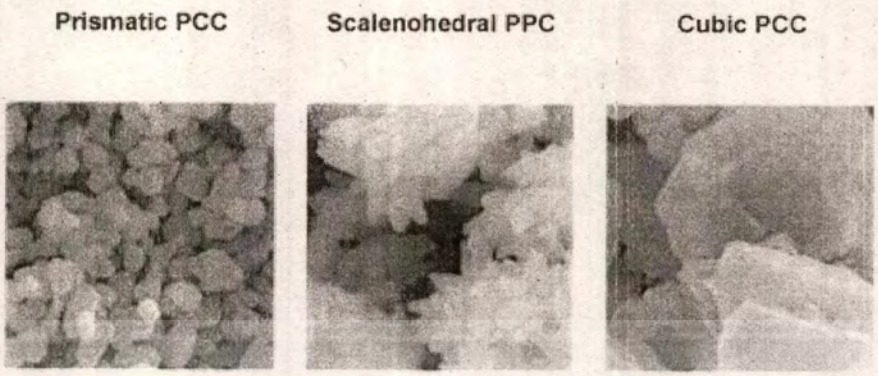


Figure 2.8: SEM images of calcite (prismatic, scalenohedral and cubic)

The chemical and physical properties of calcium carbonate do not vary greatly among the polymorphs. Aragonite has a slightly higher density than calcite and is also slightly more soluble. All PCC polymorphs exhibit high chemical purity, provided the quality of the lime or calcium hydroxide starting material is sufficient. Because of this, PCC whiteness and brightness is often unmatched, and these pigments provide high performance and good value, especially in paper applications. The clean surface resulting from the PCC precipitation process causes PCC to exhibit a slight positive surface charge, typically in the range +10 to +25 mV or higher. This is called the zeta-potential, and a positive zeta potential is particularly useful in paper filling applications. Since cellulose pulp fiber in water carries a slight negative charge and "opposites attract," using PCC often allows the papermaker to reduce the amount of chemicals needed to cause mineral fillers to be retained in the paper making process. This is a direct cost savings. The clean surface also allows PCC to be easily and efficiently treated with chemicals to enhance its performance. PCC is often more compatible with optical brightening agents or other papermaking additives than other mineral pigments.

2.6.1.1 General Calcite Information [16, 17]

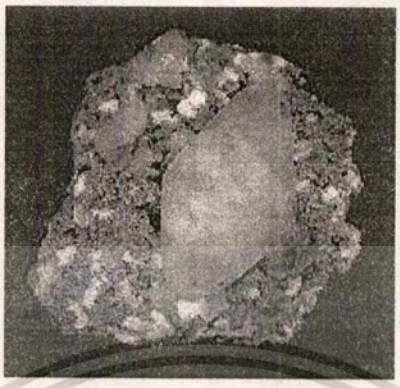


Figure 2.9: Calcite in nature

- **Chemical Formula:** $CaCO_3$
- **Composition:** Molecular Weight = 100.09 gm

40.04 % Ca	56.03 % CaO
12.00 % C	43.97 % CO_2
47.96 % O	
---	---
100.00 %	100.00 % = Total Oxide

- **Empirical Formula:** $Ca(CO_3)$
- **Environment:** Found in sedimentary, igneous, and metamorphic rocks.
- **Locality:** Common world wide.
- **Name Origin:** From the Latin, calx, meaning lime.

- **Calcite Crystallography**
- **Axial Ratios:** a:c = 1:3.41992
- **Cell Dimensions:** a = 4.989, c = 17.062, Z = 6; V = 367.78 Den(Calc)= 2.71

- **Crystal System:** Trigonal - Hexagonal Scalenohedral H-M Symbol (3 2/m)

  Space Group: R 3c

- **X Ray Diffraction:** By Intensity (I/I_o): 3.035(1), 2.095(0.18), 2.285(0.18)
- **Forms:** [2 1 1] [0 1 1]

- **Physical Properties of Calcite**
- **Cleavage:** [1011] Perfect, [1011] Perfect, [1011] Perfect
- **Color:** Colorless, White, Pink, Yellow, Brown.
- **Density:** 2.71
- **Diaphaniety:** Transparent to translucent to opaque
- **Fracture:** Brittle - Conchoidal - Very brittle fracture producing small, conchoidal fragments.
- **Habit:** Crystalline - Coarse - Occurs as well-formed coarse sized crystals.
- **Habit:** Massive - Uniformly indistinguishable crystals forming large masses.
- **Habit:** Stalactitic - Shaped like pendant columns as stalactites or stalagmites (e.g. calcite).
- **Hardness:** 3 - Calcite
- **Luminescence:** Fluorescent.
- **Luster:** Vitreous (Glassy)
- **Streak:** white

2.6.1.2 General Aragonite Information [18, 19]

Figure 2.10: Aragonite in nature

- **Chemical Formula:** $CaCO_3$
- **Composition:** Molecular Weight = 100.09 gm

40.04 % Ca	56.03 % CaO
12.00 % C	43.97 % CO_2
47.96 % O	
-------	-------
100.00 %	100.00 % = Total Oxide

- **Empirical Formula:** $Ca(CO_3)$
- **Locality:** Aragon (Spain)

- **Aragonite Crystallography**
- **Axial Ratios:** a:b:c =0.6223:1:0.7205
- **Cell Dimensions:** a = 4.959, b = 7.968, c = 5.741, Z = 4; V = 226.85

  Den(Calc)= 2.93

- **Crystal System:** Orthorhombic – Dipyramidal H-M Symbol (2/m 2/m 2/m)

  Space Group: Pmcn

- **X Ray Diffraction:** By Intensity (I/I_o): 3.396(1), 1.977(0.65), 3.273(0.52)

- **Forms:** [0 0 1] [0 1 1] [0 1 0] [1 1 0]

- **Physical Properties of Aragonite**

- **Cleavage:** [010] Distinct

- **Color:** Colorless, White, Gray, Yellowish white, Reddish white.

- **Density:** 2.93

- **Diaphaniety:** Transparent to translucent

- **Fracture:** Sub Conchoidal - Fractures developed in brittle materials characterized by semi-curving surfaces.

- **Habit:** Columnar - Forms columns

- **Habit:** Fibrous - Crystals made up of fibers.

- **Habit:** Pseudo Hexagonal - Crystals show a hexagonal outline.

- **Hardness:** 3.5-4 - Copper Penny-Fluorite

- **Luminescence:** None.

- **Luster:** Vitreous (Glassy)

- **Streak:** white

2.6.1.3 General Vaterite Information [20]

Figure 2.11: Vaterite in nature

- **Chemical Formula:** $CaCO_3$
- **Composition:** Molecular Weight = 100.09 g

  40.04 % Ca 56.03 % CaO

  12.00 % C 43.97 % CO_2

  47.96 % O

  ------- -------

  100.00 % 100.00 % = Total Oxide
- **Empirical Formula:** $Ca(CO_3)$
- **Vaterite Crystallography**
- **Axial Ratios:** a:c = 1:2.37981
- **Cell Dimensions:** a = 7.135, c = 16.98, Z = 12; V = 748.61 Den(Calc)= 2.66
- **Crystal System:** Hexagonal - Dihexagonal Dipyramidal H-M Symbol

  (6/m 2/m 2/m) Space Group: P 6_3/mmc
- **X Ray Diffraction:** By Intensity (I/I_o): 2.73(1), 3.3(1), 3.58(1)
- **Color:** Colorless.
- **Density:** 2.54

- **Diaphaniety:** Transparent
- **Hardness:** 3 - Calcite
- **Streak:** white

Table 2.6: Availability of calcium carbonate crystals

	Biological	Non-biological
Calcite (C)	very common	very common
Aragonite (A)	very common	rare
Vaterite (V)	rare	very rare
Non-crystalline $CaCO_3$	rare	non-existent

X-ray diffraction is used to determine crystalline structure. Figure 2.9 shows the comparison of XRD peaks from the database for all three crystalline structures present in Calcium carbonate.

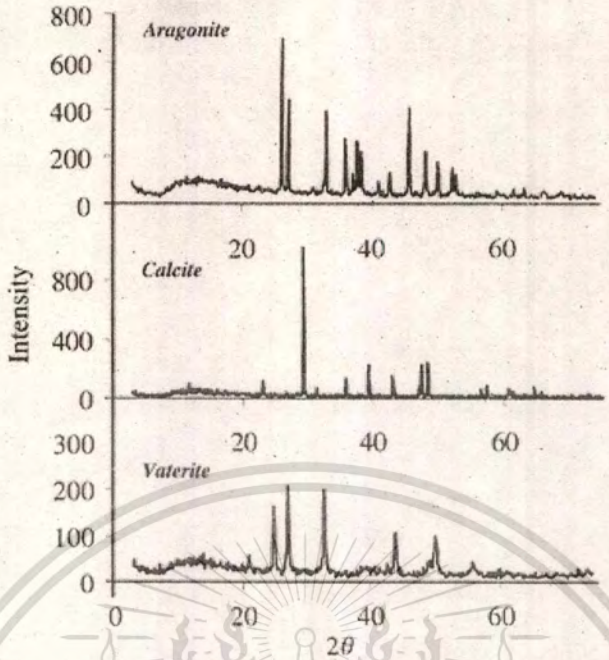


Figure 2.12: XRD Data for calcite, aragonite and vaterite

2.6.2 Production of precipitated calcium carbonate [13]

Precipitated calcium carbonate can currently be produced by three different processes:

1. Lime soda process
2. Calcium chloride process
3. Carbonation process

In the lime soda process, calcium hydroxide is reacted with sodium carbonate to produce a sodium hydroxide solution, from which the calcium carbonate is precipitated. This process is commonly used by alkali manufacturers, for whom sodium hydroxide recovery is the main objective, and the coarse PCC produced is only a by-product. In the calcium chloride process, calcium hydroxide is reacted with ammonium chloride, forming ammonia gas and a calcium chloride solution. After purification, this solution is reacted with sodium carbonate to form a calcium carbonate precipitate and a sodium chloride solution. This process is the simplest of the

three but requires a low cost source of calcium chloride to be economical. Therefore, it is usually conducted in a satellite facility adjacent to a Solvay process soda ash plant.

The third and most widely used process is the carbonation process because it can use cheap raw material.

2.6.2.1 Uses [21]

- **Use of PCC in the Paper Industry:**

With the alkaline conversion of the uncoated free-sheet market and the continuing trend toward alkaline vs. acid process papermaking in the coated, ground wood and paperboard markets, PCC is well established as a filler and coating pigment for premium quality paper products. PCC is typically produced in slurry form at satellite plants located near paper mills. PCC enhances optical properties and print characteristics of paper products, improves paper machine productivity and can reduce papermaking costs through the replacement of more expensive pulp fiber and optical brightening agents. Constantly improving quality targets make paper, and thus PCC, brightness an increasingly important factor.

- **Use of PCC in Polymer Applications:**

PCC also finds many industrial uses, based on the ability to achieve small particle sizes and special crystal shapes. In rigid PVC, such as vinyl siding and fencing, PCC increases impact strength, with some of the smaller particles able to replace expensive impact modifiers. Nano PCCs (less than 0.1 micron in size) control viscosity and sag in automotive and construction sealants, such as PVC plastisols, polysulfides, urethanes and silicones. In paint, PCC's unique particle shapes improve hiding and allow reductions in titanium dioxide levels.

- **Use of PCC in Healthcare Applications:**

An effective acid neutralizer, PCC is often used in calcium-based antacid tablets and liquids. Being high in calcium content, PCC enables the formulation of high dosage calcium supplements and multi-vitamin/mineral tablets. The small particle sizes and special particle shapes contribute to the development of good tasting calcium fortified foods and beverages.

Part II. Synthesis Method

2.7. Methods of Synthesis of Nanoparticles [22]

Major efforts in nanoparticle synthesis can be grouped into two broad areas:

1. Gas phase synthesis
2. Sol-gel processing

Nanoparticles with diameters ranging from 1 to 10 nm with consistent crystal structure, surface derivatization, and a high degree of monodispersity have been processed by both gas-phase and sol-gel techniques. Typical size variances are about 20%; however, for measurable enhancement of the quantum effect, this must be reduced to less than 5% (Murray et al. 1993).

Initial development of new crystalline materials was based on nanoparticles generated by evaporation and condensation (nucleation and growth) in a subatmospheric inert-gas environment. Various aerosol processing techniques have been reported to improve the production yield of nanoparticles. These include synthesis by combustion flame; laser ablation; chemical vapor condensation; spray pyrolysis; electrospray; and plasma spray.

Sol-gel processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and hydrothermal treatment. Size distribution of

semiconductor, metal, and metal oxide nanoparticles can be manipulated by either dopant introduction or heat treatment. Better size and stability control of quantum-confined semiconductor nanoparticles can be achieved through the use of inverted micelles, polymer matrix architecture based on block copolymers or polymer blends, porous glasses, and ex-situ particle-capping techniques.

Additional nanoparticle synthesis techniques include sonochemical processing, cavitation processing, microemulsion processing, and high-energy ball milling. In sonochemistry, an acoustic cavitation process can generate a transient localized hot zone with extremely high temperature gradient and pressure. Such sudden changes in temperature and pressure assist the destruction of the sonochemical precursor (e.g., organometallic solution) and the formation of nanoparticles. The technique can be used to produce a large volume of material for industrial applications.

In hydrodynamic cavitation, nanoparticles are generated through creation and release of gas bubbles inside the sol-gel solution. By rapidly pressurizing in a supercritical drying chamber and exposing to cavitational disturbance and high temperature heating, the sol-gel solution is mixed. The erupted hydrodynamic bubbles are responsible for nucleation, growth, and quenching of the nanoparticles. Particle size can be controlled by adjusting the pressure and the solution retention time in the cavitation chamber.

Microemulsions have been used for synthesis of metallic, semiconductor, silica, barium sulfate, magnetic, and superconductor nanoparticles. By controlling the very low interfacial tension ($\sim 10^{-3}$ mN/m) through the addition of a cosurfactant (e.g., an alcohol of intermediate chain length), these microemulsions are produced spontaneously without the need for significant mechanical agitation. The technique is useful for large-scale production of nanoparticles using relatively simple and inexpensive hardware.

Finally, high energy ball milling, the only top-down approach for nanoparticle synthesis, has been used for the generation of magnetic, catalytic, and structural nanoparticles. The technique, which is already a commercial technology, has been considered dirty because of contamination problems from ball-milling processes. However, the availability of tungsten carbide components and the use of inert atmosphere and/or high vacuum processes have reduced impurities to acceptable levels for many industrial applications. Common drawbacks include the low surface area, the highly polydisperse size distributions, and the partially amorphous state of the as-prepared powders.

2.8. Nano Precipitated Calcium Carbonate (NPCC) [24]

NPCC, also called ultrafine calcium carbonates, is one kind of new functional packing material. This is an order of magnitude smaller than the so-called ultrafine ground calcium carbonates, which are typically 0.7 microns. PCC tightly controlled precipitation process results in ultrafines that are uniform in shape, size and particle size distribution. PCC nanoparticles (<100 nm) have shown many unique properties compared to regular PCC particles (1-3 μm).

2.8.1 Uses

- **Nano PCCs For Sealant Rheology and Reinforcement**

With these extremely small particles, true thixotropic structure can be built in a sealant or other moderately to highly filled product in which control of viscosity, sag, slump and other rheological properties is needed. These ultrafine PCC particles also act as a semi-reinforcing filler, for strong physical performance. PVC plastisols, urethanes, silicones, polysulfides, and silylated polyethers are some of the types of high performance, long-lived automotive and construction sealants that use nano PCCs.

- **Nano PCCs For Rigid PVCs**

In rigid polyvinyl chloride, nano PCCs can act as impact modifiers, providing the impact strength, even at very low temperatures, needed for PVC window profiles (which are used to form the frame of vinyl windows). When formulating with a nano PCC, replacing a larger sized ground calcium carbonate (GCC), the amount of expensive acrylic or chlorinated polyethylene (CPE) impact modifier used can be substantially reduced, saving money. Nano PCCs also give the highest gloss and best surface finish to PVC window profile extrusions.

- **Other Uses For Nano PCCs**

Nano PCCs are also used in lithographic or offset inks. In highly filled litho inks, they can serve as the main rheological additive and cost-reducing filler. In lightly filled offset inks, they can extend other more expensive thickeners, as well as replace oils and varnishes. Nano PCCs thicken PVC plastisol silk screen inks. Gravure inks need very low abrasion fillers. Small particle-sized PCC is excellent here.

Rheology and filling are also the reasons to use ultrafine PCCs in epoxy and other adhesives, as well as in unsaturated polyester gel coats. Other uses include:

- High strength reinforcement of rubber
- Detackification and mold release for thin gauge surgical and other medical gloves
- Nucleating agent in emulsion polymerization
- Carrier for catalysts, peroxides, fragrances
- Powder flow control additive for acrylic modifiers and other sticky products.

The uncoated nano PCC products can be used for fortifying beverages such as cow's milk and soy milk. By using a calcium carbonate with a very small particle size, the calcium fortifier stays suspended much longer, making a better tasting and appearing product.

Ultrafine PCCs are often coated with a low percentage (1-3 percent) of a fatty acid, such as stearic acid, or other organic material, for use in non-aqueous systems like plastics, rubber and sealants. These coatings increase the dispersibility of the PCC in the system's polymer and its compatibility with the polymer, which maximizes the rheological and / or reinforcing efficiency of the PCC.

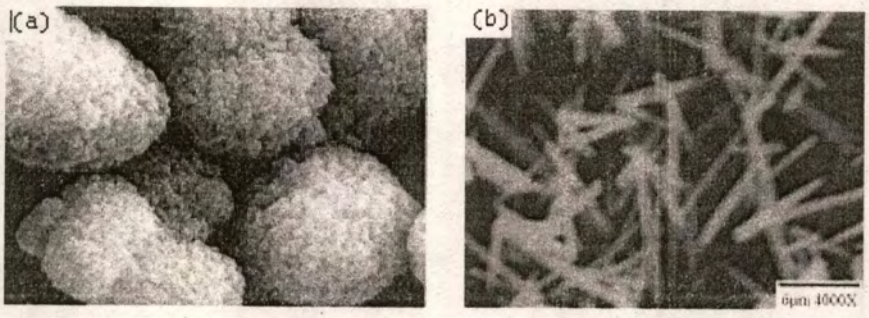
The choice of coating depends on the type of polymer the ultrafine PCC will be used in and the type of rheology desired. As polymers vary widely in polarity and solubility constants, different organics are chosen to give the best compatibility and/or the best balance of rheological and physical properties. Two ultrafine PCCs coated with the same amount of different organic materials can produce very different viscosities, degrees of shear thinning, and controls of sag and slump.

Part III. Literature Review

2.9. Literature Review

Kovacevic et al. [24] found calcium carbonate nanocomposites exhibit unique and improved properties in polymer composites appeared. In poly (vinyl acetate) (PVAc) matrix, the morphology of the composite was found to be dependent on the filler particle size. The nanoparticles form a 'net like' dispersion in the matrix, whereas the particles in the micron scale formed 'islands'. Qui et al. [25] studied the application of $CaCO_3$ nanoparticles as additives in lubricating oils. It was found that $CaCO_3$ nanoparticles exhibited good load-carrying capacity, antiwear and friction-reducing properties.

Thus far, there is little evidence of an optimized method to control size and morphology of PCC particles. Current methods used make it difficult to predict particle size and morphology and require large amounts of energy. Studies have been done on the use of LEM for the production of nanoparticles [26], such as calcium phosphate fine particles. However, these studies used surface chemistry such as surfactant adsorption and phase stability to control the particle size and shape, which is different from the route using mass restriction and kinetic control for synthesis.



Figures 2.13: (a) and (b) show some examples of SEM images of PCC particles of different morphology. However these are not nanoparticles.

2.9.1 Methods of Synthesis of Calcium carbonate Nanoparticles

There are various methods for the synthesis of nanoparticles. A nanophase material synthesized by gas evaporation is one of the methods, and was introduced by Granqvist and Burman [1]. However, thermal evaporation is a known limitation to this method for metals and intermetallic compounds. This was later overcome by Hahn and Averback [2], by substituting the thermal evaporation source with a sputtering source, thus enabling the synthesis of nanoparticles. However, the size of the particles depended on pressure of Ar in the operating chamber. Small changes in pressure would change the particle size.

Liu et al. [27] prepared nanosized $CaCO_3/SiO_2$ composite particles by the sol-gel process of $CaCO_3$ and Na_2SiO_3 in an agitated tank reactor, with an average composite size of sol-gel coated $CaCO_3$ of about 40 nm. $CaCO_3$ nanoparticles have also been prepared using a microemulsion technique consisting of sodium dodecyl-sulphate (SDS)/isopentanol/cyclohexane /water, [25].

Zhang et al. [28] synthesized nanoparticles of calcium carbonate in the reaction system of $Ca(OH)_2$/-H_2O-CO_2. It was reported that the increase in temperature and mass fraction of the $Ca(OH)_2$ suspension increased the particle size of the final product.

McCormick et al. [3] applied mechanochemical synthesis by placing $CaCl_2$, Na_2CO_3 and NaCl in a ball miller and obtained $CaCO_3$ in a NaCl matrix. One disadvantage of mechanochemical synthesis is the NaCl waste.

Liquid emulsion membranes (LEM) were first developed by Li at Exxon [29]. One of the advantages of using LEM is that it can be designed to be highly selective depending on the purpose required. Some other advantages of using LEM is the low cost of operation since the organic (oil) layer can be reused, and has a high separation rate due to the high surface area. Hirai et al, [26] reported that LEM can be used to synthesize spherical calcium phosphate particles. One disadvantage of LEM is the emulsion becomes unstable after prolonged contact with the feed solution and high speed mixing. Gupta et al. [4] modified LEM to be two separate water/oil emulsions, called double water in oil emulsion method. Although this method used lower cost of production (comparing to LEM) as well as overcame the problem of an unstable external phase of LEM, but formed larger particles than expected.

Wang et al. [30] synthesized nanometer size PCC (15-40 nm) using a lime suspension in a rotating packed bed reactor and had a very narrow distribution. It was reported that the most important stage for controlling the carbonation rate was the absorption of CO_2. However, it was later discovered to be controlled by dissolution of $Ca(OH)_2$. This method is also known as "high gravity multiphase reactive precipitation." The method required a high acceleration centrifuge to create the high gravity above the gravity of the earth. This required expensive synthesis

equipment. However they also reported that the shape (spherical or needle like) and morphology could be controlled.

Tsuzuki et al. [31] synthesized calcium carbonate nanoparticles using a mechanochemical reaction followed by heat treatment. A solid-state displacement reaction would occur during mechanical milling of the reaction powder mixture. The heat treatment ensured completion of the reaction. This limited the morphology of the particle to calcite, and had a high energy consumption. Mechanical milling causes irregularities in particle shape and distribution.

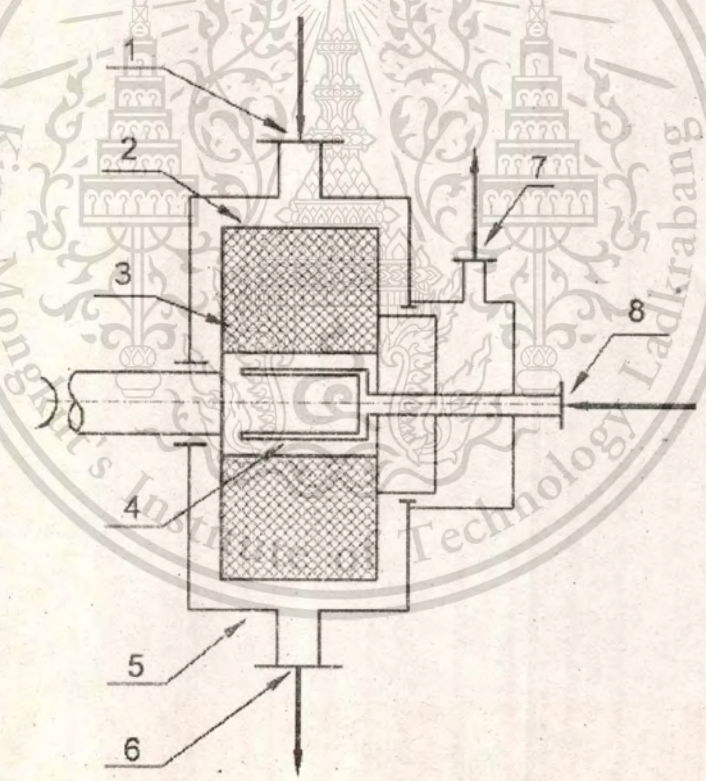
2.9.2 High gravity reactive precipitation (HGRP) [5]

High gravity technology, also called Higee technology, carried out in a rotating packed bed (RPB), was originally invented in 1979 for the separation processes by Ramshaw. The first large-scale application of RPB as a reactor took place in China in the production of nano $CaCO_3$ by HGRP using carbon dioxide and lime. Uniform, small particles were produced in the RPB due to the presence of a sharp super-saturation interface accompanied by the very short liquid residence time in the device.

RPB consists mainly of a rotating packed rotator inside a stationary casing. The high gravity environment created by the RPB, which could be orders of magnitude larger than gravity, causes aqueous reactants going through the packing to spread or split into micro or nano droplets, threads or thin films, thus markedly intensifying mass transfer and micromixing to the extent of 1 to 3 orders of magnitude larger than that in a conventional packed bed.

The structure of a typical countercurrent RPB is illustrated in Fig. 2.14. The key part consists of a packed rotator (2). The liquid distributor (4) consists of two pipes, each with a length

to cover exactly the axial depth of the packed section of the rotator. The rotator is installed inside a stationary casing (5) and it rotates at a speed of several hundred to several thousand rpm. Liquid, or slurry is introduced into the eye space of the rotator from the liquid inlet pipe (8) to spray onto the inside edge of the rotator through a slotted pipe distributor. The liquid entering the bed flows in the radial direction under centrifugal force, passing through the packing and outside space between the rotator and the casing, to finally collect and leave the RPB via the liquid outlet (6). Gas is introduced from an outside source, e.g., a gas cylinder, through the gas inlet (1), to flow inward countercurrently against the liquid in the packed section of the rotator, and finally out from the gas outlet (7).



Figures 2.14: The structure of a countercurrent RPB (1) gas inlet; (2) rotator; (3) packing; (4) liquid inlet

The basic principle of high gravity technology is to create a high-gravity environment via the action of centrifugal force, and it therefore differs from conventional multiphase separation or differential density separation dependent on earth's gravitation. Its essence lies in the tremendous intensification of mass transfer and micromixing. The fluids going through the packing are spread or split into micro or nano droplets, threads or thin films under the high-gravity environment in a RPB, to the order of several hundred or even several thousand times larger than the gravitational acceleration of the earth. The rate of mass transfer between gas and liquid in a RPB is therefore 1 to 3 orders of magnitude larger than that in a conventional packed bed.

It was reported that nanoparticles of $CaCO_3$ of a mean size less than 100 nm could not be produced by the conventional precipitation technology if no agents were added for the restraint of crystal growth. On the contrary, the mean size of $CaCO_3$ particles can be adjusted and controlled from about 15 to 30 nm by this HGRP technology, without addition of any crystal growth inhibitor. Moreover, the shape of nano $CaCO_3$ can be controlled precisely by employing appropriate crystal morphology controlling agents in the HGRP technology

*2.9.2.1 **Analysis of kinetics** [5, 13]*

A precipitation process consists of three main steps:

1. Chemical reaction
2. Nucleation
3. Crystal growth

If agglomeration and ripening mechanisms are neglected, precipitation mechanisms can be described by:

$A + B \rightarrow P$ (Reaction) (1)

$P + P + ... + P \rightarrow P^*$ (Nucleation) (2)

$P^* + P \rightarrow P_1$

$P_1 + P \rightarrow P_2$

..... (Crystal growth) (3)

$P_{n+1} + P \rightarrow P_n$

where

A is reactant (here, CO_2)

B is reactant (here, $Ca(OH)_2$)

P is product (here, $CaCO_3$)

P* is crystal embryo

$P_1 \ldots P_n$ are crystals of different sizes

These mechanisms are quite similar to that of polymerization. The particle size distribution (PSD) of the product depends on each step. In general, reaction and nucleation are both relatively fast, while crystal growth proceeds slower. The kinetic equations of the three steps are often described as follows:

$$dc_p / dt = kc_A^{\alpha} c_B^{\beta} \quad (4)$$

$$dn / dt = k_N(c_p - c^*)^m \quad (5)$$

$$dl / dt = k_g(c_p - c^*)^{\gamma} \quad (6)$$

where:

c_p is concentration of P

c_A is concentration of A

c_B is concentration of B

c* is supersaturation concentration, mol/m^3

k_N is constant of nucleation rate

k_g is constant of crystal growth rate

l is characteristic size of crystal, m; or liquid phase

α,β are orders of reaction

m is nucleation rate order

γ is order of growth

The growth order γ is usually in the range of between 1 and 2. In the preparation of ultrafine particles via reactive precipitation, the chemical reaction is sufficiently fast that a high degree of supersaturation of P is achieved in local volumes. This causes the formation of crystals to be dominated by homogenous nucleation, with the nucleation order m in the range of 5 to 18. The values of reaction order alpha and beta are often more than 2. Therefore, a high concentration of product C_p favors an increase in the number of nuclei and a decrease in average particle size because nucleation depends more strongly on C_p than do the reaction and crystal growth.

A high degree of supersaturation, uniform spatial concentration distributions and identical growth time for all crystals are essential conditions for the synthesis of nanoparticles with narrow size distribution. The induction time, τ, as the time from the first creation of the conditions for homogeneous nucleation to that of the establishment of a steady-state nucleation rate, can be estimated by the equation given by Dirksen and Ring:

$$\tau = \frac{6d^2 n^*}{(D \ln S)} \qquad (7)$$

where

d is the diameter of molecules

n* is the number of ions embodied in a crystal embryo

D is the coefficient of diffusion

S is the ratio of supersaturated concentration to saturated concentration

In aqueous solutions, τ is on the order of 1 ms or less.

For homogenous nucleation, tiny variations of c_p lead to a large change of nucleation rate due to the high value of m (see Eq. 5). As a result, the PSD is broad if the spatial concentration distribution in the reactor is non-uniform. In addition, differences of growth time of crystals in the reactor broaden the PSD. Therefore, to obtain nanoparticles with a narrow size distribution, one should do as much as possible to meet the requirements of: (a) high degree of supersaturation, (b) spatially uniform concentration, and (c) the same growth time for all crystal.

Experimental results reported by Chen et al. and Tosun showed that micromixing (mixing on the molecular scale) and macromixing (mixing on the vessel scale, local or overall) have a significant effect on the particle size distribution (PSD) in the reactive precipitation between $BaCl_2$ solution and Na_2SO_4 solution. Uniform spatial concentration distribution of any component on the vessel scale can only be achieved by macromixing. Uniform spatial concentration distribution on the molecular scale can only be reached by intense micromixing. Both macromixing and micromixing can occur simultaneously in the vessel. Micromixing is a key factor in determining the degree of the supersaturation concentration of the solute and its local spatial distribution.

From the viewpoint of chemical reaction engineering, the reaction rate and subsequent nucleation in precipitation will be controlled by the intrinsic kinetics without the influence of micromixing in the region of $t_m < \tau$, and controlled or influenced by micromixing when $t_m > \tau$, where t_m is the characteristic time of micromixing for species reaching a maximum mixed state at the molecular level. Because of the very strong nonlinearity of homogeneous nucleation, intensification of micromixing to reach the region of $t_m < \tau$ should be taken so that the rates of nucleation at different locations in a precipitator will be nearly the same, and the PSD can thus be controlled at a uniform level. The characteristic micromixing time can be estimated by the equation:

$$t_m = k_m (\nu / \varepsilon)^{1/2} \tag{8}$$

where k_m is a constant. Whereas its value has been given variously by different researchers; here k_m=16. As an example, in a common stirred tank, the value of the energy dissipation rate, ε, is on the order of 0.1-10 w-kg^{-1}, and that of kinematic viscosity, υ, is 1×10^{-6} m^2.s^{-1} in aqueous solutions. In this case, the characteristic micromixing time, t_m, is estimated to be on the order of 5-50 ms. In aqueous solutions, the value of the nucleation induction time is often on the order of 1 ms or less. Therefore, $t_m \gg \tau$. This implies that the PSD in a stirred tank cannot be easily controlled, and the scale-up effect will play a more important role owing to the poor micromixing. Micromixing has little effect on crystal growth because of the lower rate of the latter. Only the influence of macromixing at the vessel scale should be taken into consideration. It is evident that nuclei will grow to the size of the particles with uniform size distribution only in the macro environment of uniform concentration distribution.

On the basis of the above analysis, the rules of designing a reactor to prepare nanoparticles with very narrow size distribution and controlled morphology by the precipitation technology could be proposed as follows:

(i) Separate the reaction and nucleation zones (RNZ) from the crystal growth zone (CGZ)

(ii) Locate the CGZ in a well-macromixed region

(iii) Design macro flow patterns in the RNZ as plug flow.

Following these, the optimal apparatus is the combination of a well-micromixed plug flow reactor and a well-macromixed reactor. Since mass transfer rate and micromixing in a RPB is much larger than that in a conventional packed bed, this is very helpful for the generation of higher supersaturated concentrations of the product in the precipitation process. When regarded as a mixing device, a RPB is similar to a combination of a static mixer and a stator-rotator mixer. The value of t_m in RPB is estimated to be 10-100 μs orders of magnitude, which is smaller than the typical value of the nucleation induction time of the order of 1 ms in aqueous solutions, and therefore it could meet the requirement of $t_m < \tau$ and as a result the PSD could well be controlled. Previous work by Guo has shown that the macro flow pattern in a RPB is close to that of the plug flow. Theoretically, a RPB reactor is ideal for the preparation of nanoparticles according to the above analysis. As a result, HGRP, which facilitates reactive precipitation taking place under high-gravitational conditions, is well adapted to the synthesis of nanoparticles.

2.9.2.2 Particle Size Distribution [32]

The particle size distribution (PSD) was calculated on the basis of the TEM or SEM pictures. The influences of the operation conditions, the gas flow rate, liquid flow rate, initial concentration, and rotating speed, that is, the high-gravity level on the PSD of CaCO3, were experimentally investigated without the addition of any chemical inhibitor. The effect of the high-gravity level, g_r can be estimated by the equation:

$$g_r = (N/60)^2(d_{in} + d_{out})/2$$

where

N is the rotating speed of the rotator in rpm) on the mean particle size of $CaCO_3$

d_{in} is inner diameter of the rotator(mm)

d_{out} is outer diameter of the rotator(mm)

2.9.2.3 Spinning Disc Technology [33].

The pioneering development of an intensified spinning disc reactor (SDR) has enabled research into potential areas of application for novel reactor technology to be undertaken.

The principle of operation of the SDR is based on the creation of a high acceleration field by rotation of a horizontal disc, the surface of which may be smooth or grooved.

Under the influence of the centrifugal force, the reacting fluid fed to the centre of the disc by a stationary feed pipe flows on the disc surface in the form of a thin film covered by numerous surface ripples. Experimental evidence for thin film flow on a stationary inclined plane suggests that these ripples or surface waves are probably responsible for vigorous mixing activity within the film that enhances heat and mass transfer in the fluid.

The important benefits offered by spinning-disc technology can be summed up as follows:

1. The extremely high acceleration thus generated is capable of producing very thin films in which heat transfer, mass transfer and mixing rates are likely to be greatly improved.
2. The effect of very short and controllable residence times achieved under the centrifugal action enable heat sensitive materials to be processed without risk of degradation.

3. The rotational speed of the spinning surface provides an additional degree of freedom that can be readily manipulated for optimization of equipment performance.
4. The thin film on the rotating disc is likely to have a plug-flow character, which is desirable to achieve high product throughput by limiting transfer reactions and improving control of product properties, such as the molecular weight distribution (MWD) of polymers.

The potential applications of such a high-acceleration environment in processes involving separation, heat transfer, gas-liquid reactions, crystallization, precipitation of nanoparticles, etc. have been extensively reviewed by Ramshaw. The rotating disc surface would appear to be a particularly attractive choice for systems which, in conventional reactors, are heat or mass-transfer limited. Two main categories of reactions that exhibit such characteristics are inherently fast exothermic reactions and polymerization reactions.

2.9.3 Industrial Production of Nano $CaCO_3$ Using HGRP [5]

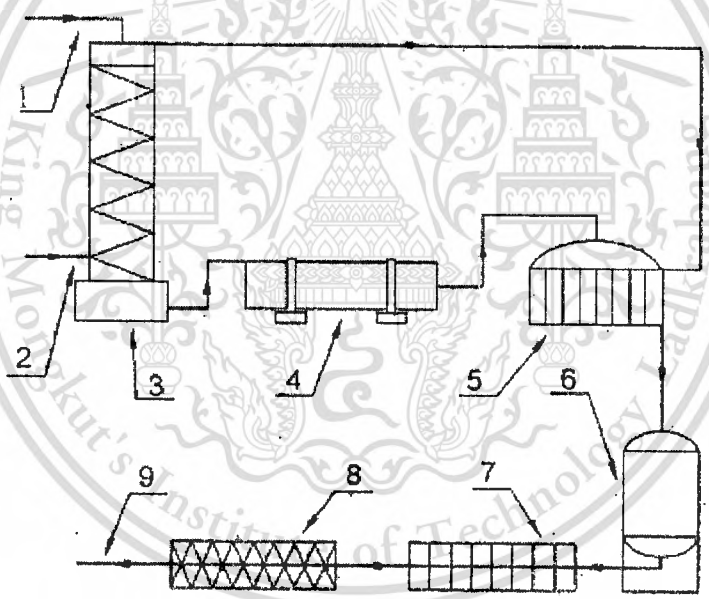
Both theoretical analysis and laboratory experiments revealed that HGRP has great potential for the preparation of nanoparticles, which led to a rapid acceptance of this technology by the nano-size $CaCO_3$ industry. At present, nano $CaCO_3$ production lines using HGRP technology have been put into operation in five enterprises in China, varying in capacity from 3,000 to 10,000 t/a. A typical production line of nano $CaCO_3$ by HGRP at Shanxi Huaxin Nanomaterials Co., Ltd. is illustrated in figures 2.15. Reactions in the production process can be written as:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Limestone and coke are dumped into the shaft kiln from the top, while air is blown into the shaft kiln from the bottom via a fan. Limestone is converted into quicklime after calcination in the shaft kiln. The quicklime enters the slaker to form lime milk, which is pumped into RPB after refining. In the shaft kiln air reacts with coke to form a kiln gas rich in CO_2. After removing soot, SO_2 and coal tar, the kiln gas is introduced into RPB to react with the lime milk to form a nano $CaCO_3$ suspension, which is subsequently pumped into the modification tank, where the nano $CaCO_3$ is upgraded and emulsified at a fixed temperature by a surface-active agent.



Figures 2.15: Production flowsheet of nano $CaCO_3$ by HGRP in Shanxi Huaxin Nanomaterials Co., Ltd. (1) limestone and coke; (2) air; (3) shaft kiln; (4) slaker; (5) RPB; (6) modification tank; (7) filter; (8) dryer; (9) nano $CaCO_3$

Modified nano $CaCO_3$ is post-treated by dewatering and drying to yield commercial nano $CaCO_3$ powders of the primary mean particle size of 30nm. No obvious scale-up effect occurs.

Industrial scale-up results indicated that production of nano $CaCO_3$ by HGRP has unique advantages over conventional technology, as summarized in Table 2.7.

Table 2.7: Comparison of the production of nano $CaCO_3$ by conventional technology

Items	Conventional technology	HGRP
Reactor types	Stirred tank or tower, bubbling reactor	RPB
Rate of micromixing	Slow, 5–50 ms	Fast, 0.01–0.1 ms
Rate of mass transfer	Slow, 1	Fast, 10–100
Product particle sizes	>100 nm without crystal growth inhibitor; <100 nm with crystal growth inhibitor. Morphology is not easy to control.	15–30 nm without crystal growth inhibitor. Morphology is controllable.
Batch reaction time	Long, 60–75 min, additional three days aging	Short, 15–25 min
Reactor volumes (3000 t/a)	30–50 m^3, 3 reactors. Investment is expensive.	About 4 m^3. Investment is cheap.
Controllability of production and production cost	Difficult, repeatability of product quality is poor, cost is high.	Easy, product quality is stable, cost is low.
Scale-up effects	Large, hard to scale up	No negative scale-up effects

Chapter 3

Experiment

3.1. Chemical and Apparatus

3.1.1 Chemical

- Calcium oxide (CaO)
- Distilled water
- Carbon dioxide (CO_2)

3.1.2 Apparatus

• pH meter	1	Set
• Hoses	3	Lines
• Reactor	1	Set
• Stirrer motor	1	Set
• Stirrer motor with paddle	1	Set
• Pump	1	Set
• Feed Tank	1	Set
• Pressure gauge	1	Set

3.2. Reactor design and Experimental setup

3.2.1 Reactor design

From the diagram of HGRP reactor shown in figure 2.14, the three dimensional form of such reactor was designed by using Microsoft Word and Googlesketchup programs.

3.2.1.1 Parts of reactor

Parts of reactor can be divided into three parts:

1. Reactor tank

Reactor tank was 3.32 liters made by stainless steel. The reactor tank (see figure 3.1) had three interesting positions: (1) gas inlet; (2) liquid outlet; and (3) gas outlet. The gas inlet as shown in figure 3.1 was a 0.0137 m in diameter. The liquid outlet was 0.03 m while gas outlet was 0.033 m in diameter.

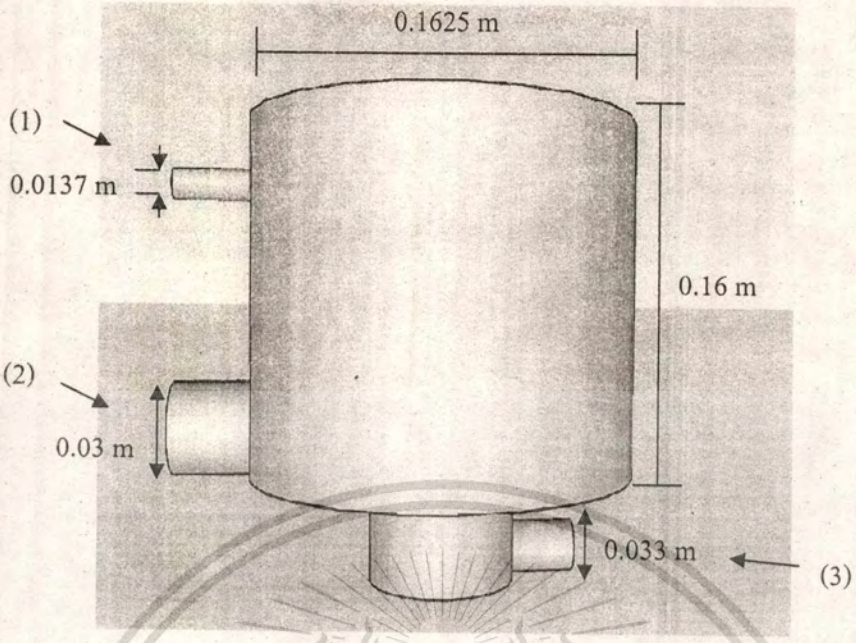


Figure 3.1: 3.32 liters -reactor tank

2. Rotational part

There are two important components in the rotational part. The first component is the rotational rod (shown in figure 3.2), used to connect between the motor and the cap of reactor tank. The second component was the metal dice capture as shown figure 3.2. It used to capture packed bed.

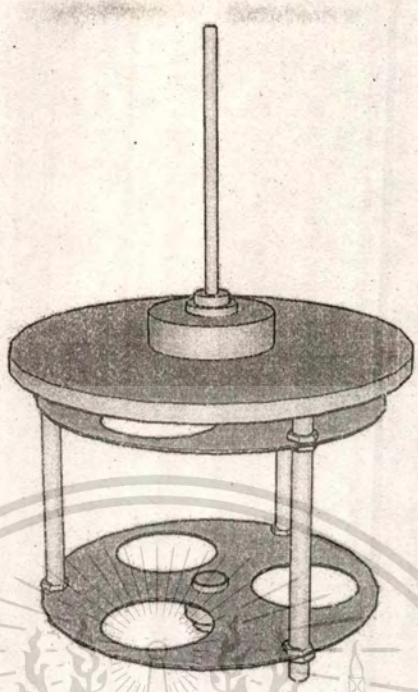


Figure 3.2: Rotational part

3. Liquid inlet

The liquid inlet as shown in figure 3.3 was a 7.29 mm in diameter of cylinder tube with several 0.06 mm punched holes.

The designed reactor made by stainless steel, was constructed by Srivisan-Kesara metal work Co., Ltd.

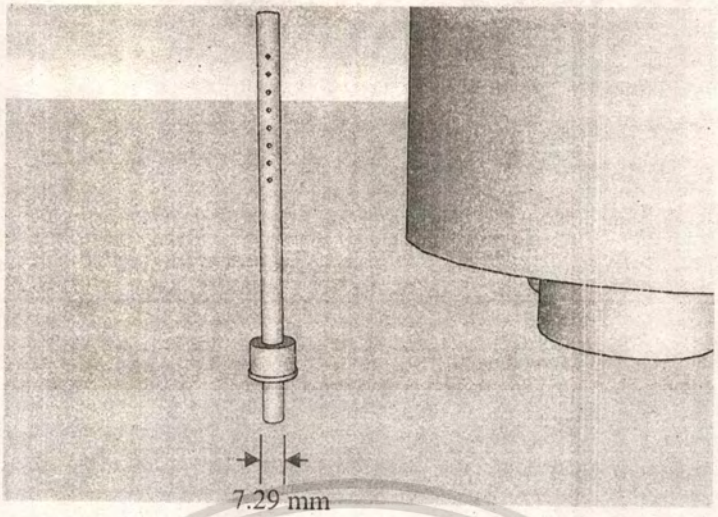


Figure 3.3: 7.29 mm Liquid inlet

3.2.2. Experimental setup

All parts of stainless steel HGRPB reactor were connected as shown below:

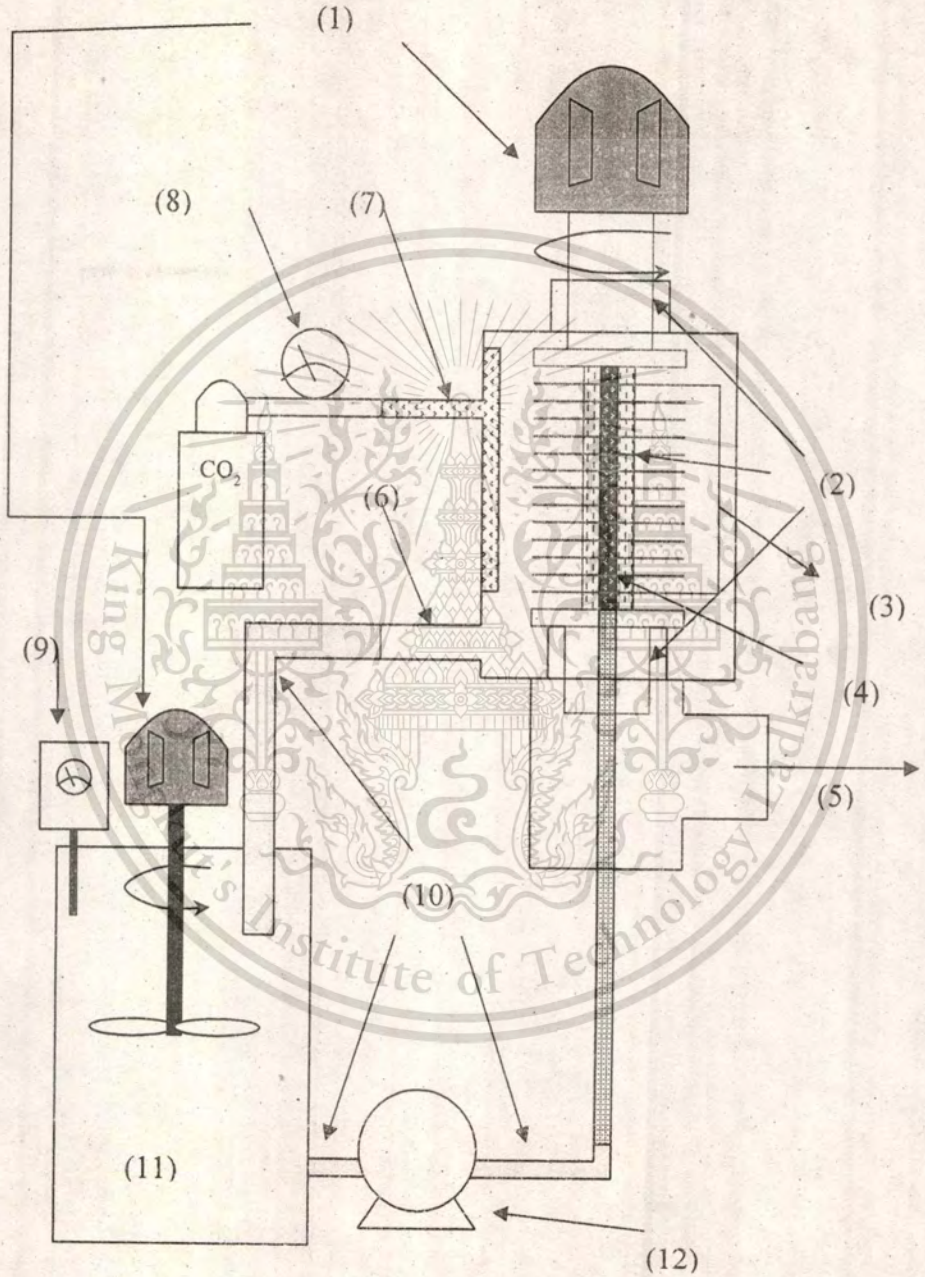


Figure 3.4: Experimental setup: (1) stirrer motor; (2) rotating core; (3) CDs packed bed; (4) punched holes; (5) gas outlet; (6) liquid outlet; (7) gas inlet; (8) pressure gauge; (9) pH meter; (10) hoses; (11) feed tank; (12) pump

3.3. Preparation of NPCC using HGRPB reactor

In the experiments, the $CaCO_3$ reaction precipitation was driven with gaseous carbon dioxide and aqueous calcium hydroxide. The aqueous solution of calcium hydroxide was prepared with distilled water.

In reaction precipitation, the feed concentration was the important operating variable to control product properties. The particle formation and growth processes in the precipitation, which depend directly on the supersaturation of solution, varied with the feed concentration.

Using the designed HGRPB reactor, the varied concentration of $Ca(OH)_2$: 2.57, 4.00, 6.12, 8.25 and 9.93 grams per 2 liter with fixed rotating speed, liquid flow rate, CO_2 pressure and temperature were investigated.

The fixed parameters were given as follows:

- Rotating speed at 2000 rpm
- Liquid flow rate at 9 liter/min
- CO_2 pressure at 10 Pa
- Temperature at room-temperature

3.4. Characterization of NPCC

The objective of this part of the experimental was to determine an effective method to measure the size of the particles synthesized NPCC and to obtain a clear image of the shape of such particles.

The following equipments were used to study the particles size during the experiment.

3.4.1 XRD

Figure 3.5: X-ray Diffractometer (XRD)

The crystal polymorphism of the NPCC powder was characterized by X-Ray Diffraction (XRD). XRD is a high-tech, non-destructive technique for analyzing a wide range of materials, including fluids, metals, minerals, polymers, catalysts, plastics, pharmaceuticals, thin-film coatings, ceramics and semiconductors.

XRD used was model D8 ADVANCE from Scientific Instruments Service Centre (SISC) of KMITL. The operating conditions of the XRD instrument such as the step range and scanning range were set at 0.020° degree/sec and 20° to 70°, respectively.

3.4.2 SEM

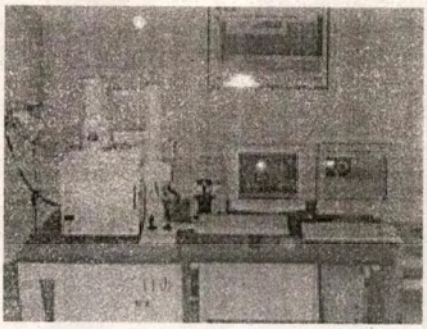


Figure 3.6: Scanning electron microscope (SEM)

The particle size and shape of resultant NPCC particles were characterized by Scanning Electron Microscope (SEM). SEM used was model LEO 1455 VP from Scientific Instruments Service Centre (SISC) of KMITL. The images were used to measure the size of 5 random particles and the average was taken as the particle size for each condition.

Chapter 4

Results and discussion

4.1. Reactor

4.1.1 Reactor design and experimental set up

HGRPB Stainless steel reactor from sketch design in figure 3.1 and the experimental setup (shown in figure 3.4) were shown in figure 4.1 and figure 4.2, respectively:

Figure 4.1: Stainless steel reactor

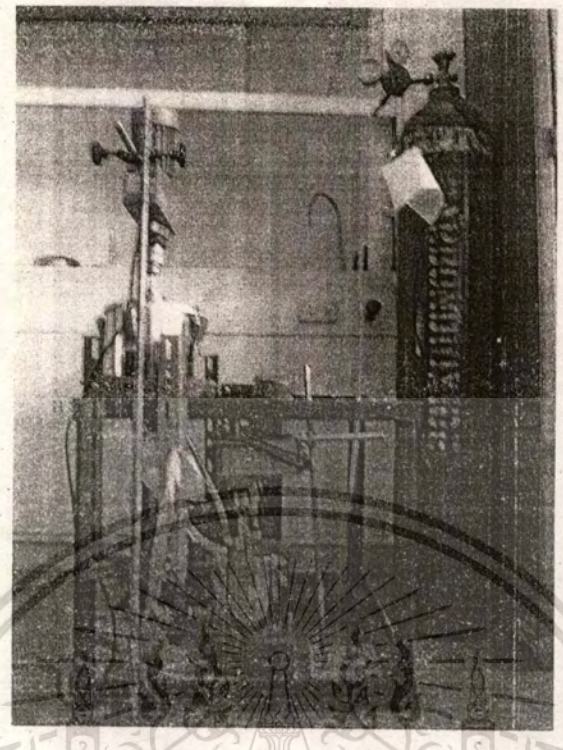


Figure 4.2: Experimental setup

4.2. Preparation of NPCC using HGRPB reactor

In preparation of NPCC using HGRPB reactor, the following parameters were fixed:

- Rotating speed at 2000 rpm
- Liquid flow rate at 9 liter/min
- CO_2 pressure at 10 Pa
- Temperature at room-temperature

and the concentration of $Ca(OH)_2$: 2.57, 4.00, 6.12, 8.25 and 9.93 grams per 2 liter were varied. The morphology of NPCC particles of each sample were examined by a scanning electron microscope. Prior to SEM examination, the samples are coated with gold to improve material

conductivity. The images of the selected SEM photograph at different concentration are shown below.

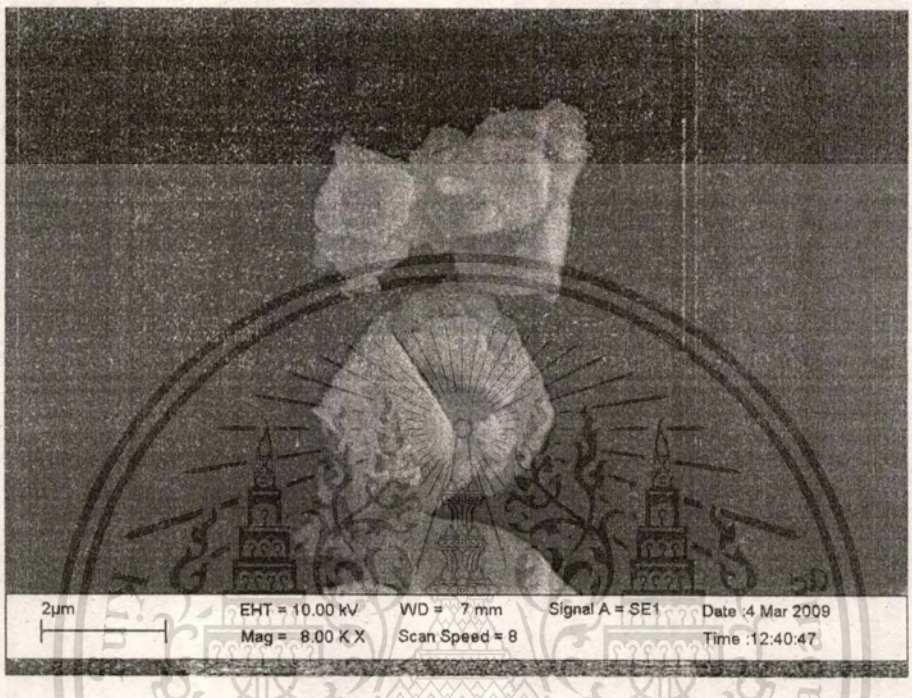


Figure 4.3: SEM image of PCC using $Ca(OH)_2$: 2.57 g / 2 L

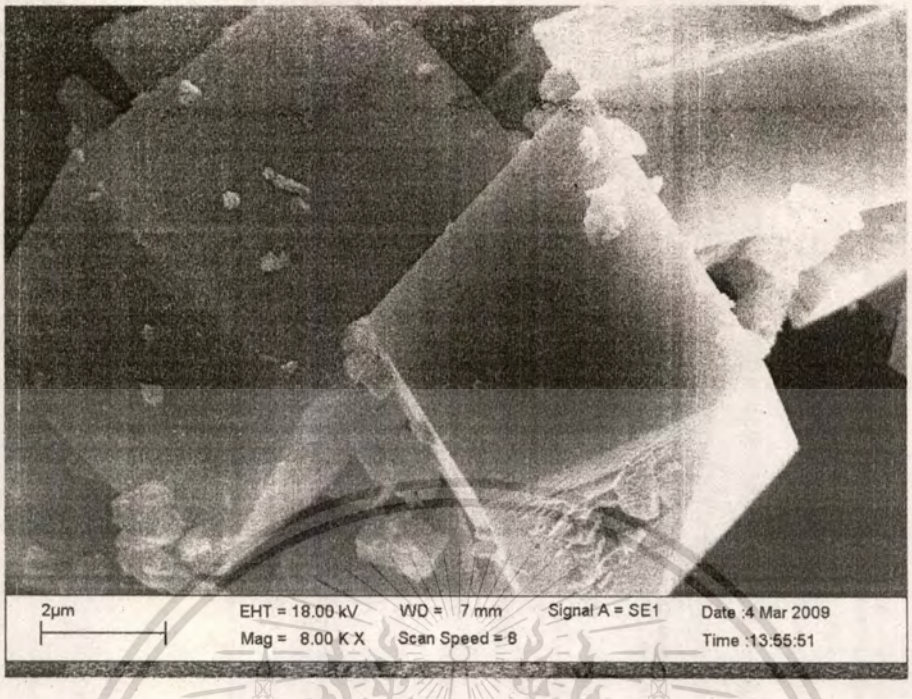


Figure 4.4: SEM image of PCC using $Ca(OH)_2$: 4.00 g / 2 L

Figure 4.5: SEM image of PCC using $Ca(OH)_2$: 6.12 g / 2 L

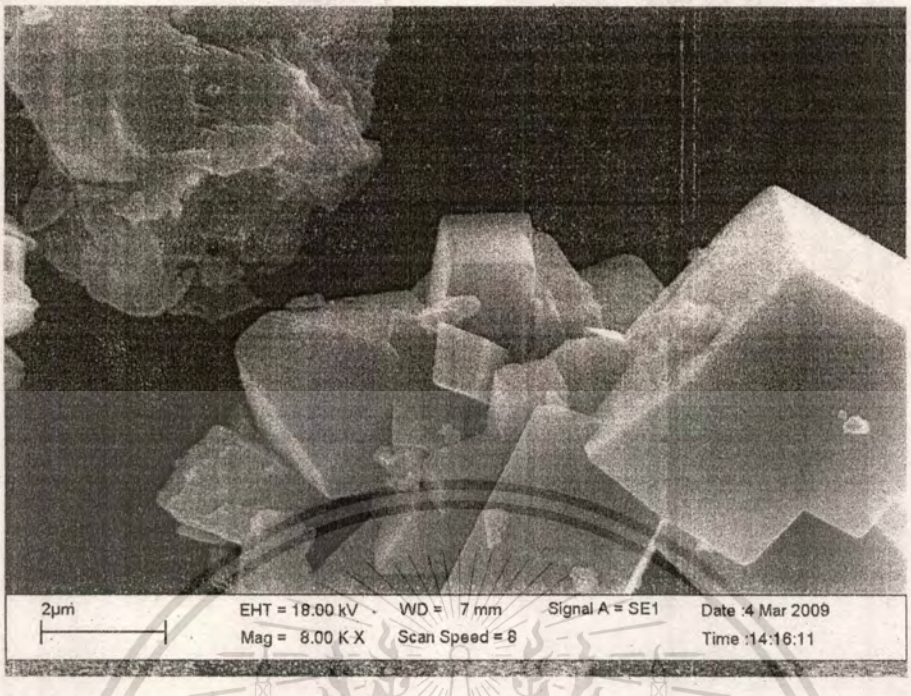


Figure 4.6: SEM image of PCC using $Ca(OH)_2$: 8.25 g / 2 L

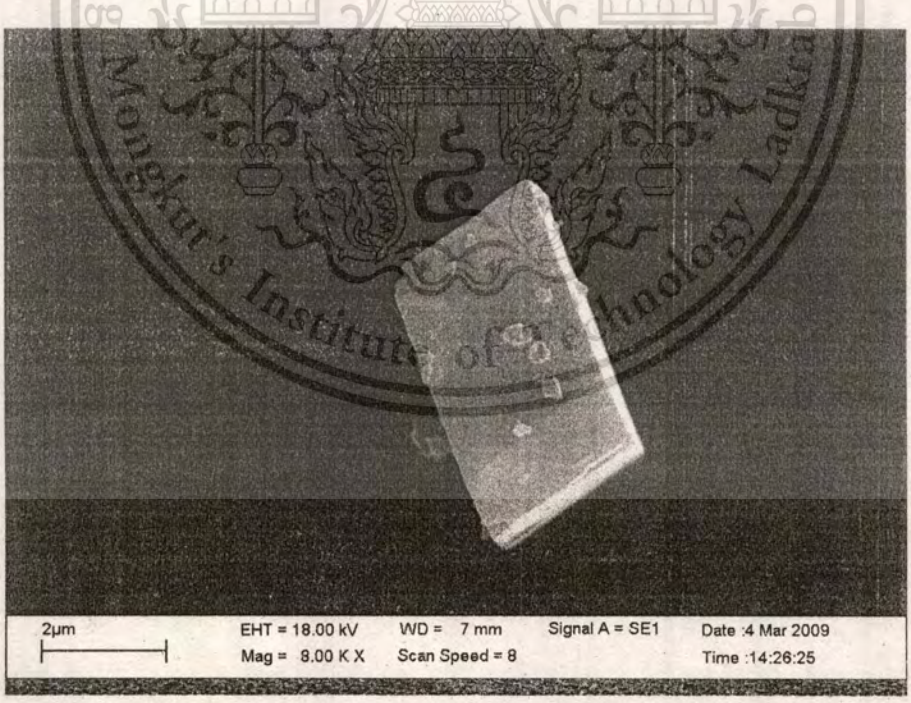


Figure 4.7: SEM image of PCC using $Ca(OH)_2$: 9.93 g / 2 L

It was observed that all the varied concentration of $Ca(OH)_2$, NPCC particles formed like cubic rhombohedral crystals with large particle size distribution. The particles were stacked randomly. The results are similar to those obtained by Chen et al. but they are 10 times larger. The variation in particle size can be explained in term of crystal growth from the limitation of rotating speed. Higher rotating speed of RPB might intensify micro-mixing and favored the formation of small particle.

4.2.4 XRD Study

The XRD patterns of NPCC powder were shown in figure 4.8 - 4.12. They agreed with that of the calcite crystal structure in the JCPDS database. The characteristic diffraction peaks attributable to calcite at (2θ) 29.5°, 47.3°, and 48.6° (corresponding to a set of d-spacing of 3.02, 1.92, and 1.87 nm, respectively) were unambiguously distinguishable as marked by the asterisks in the plot, in good agreement with the literature data for calcite.

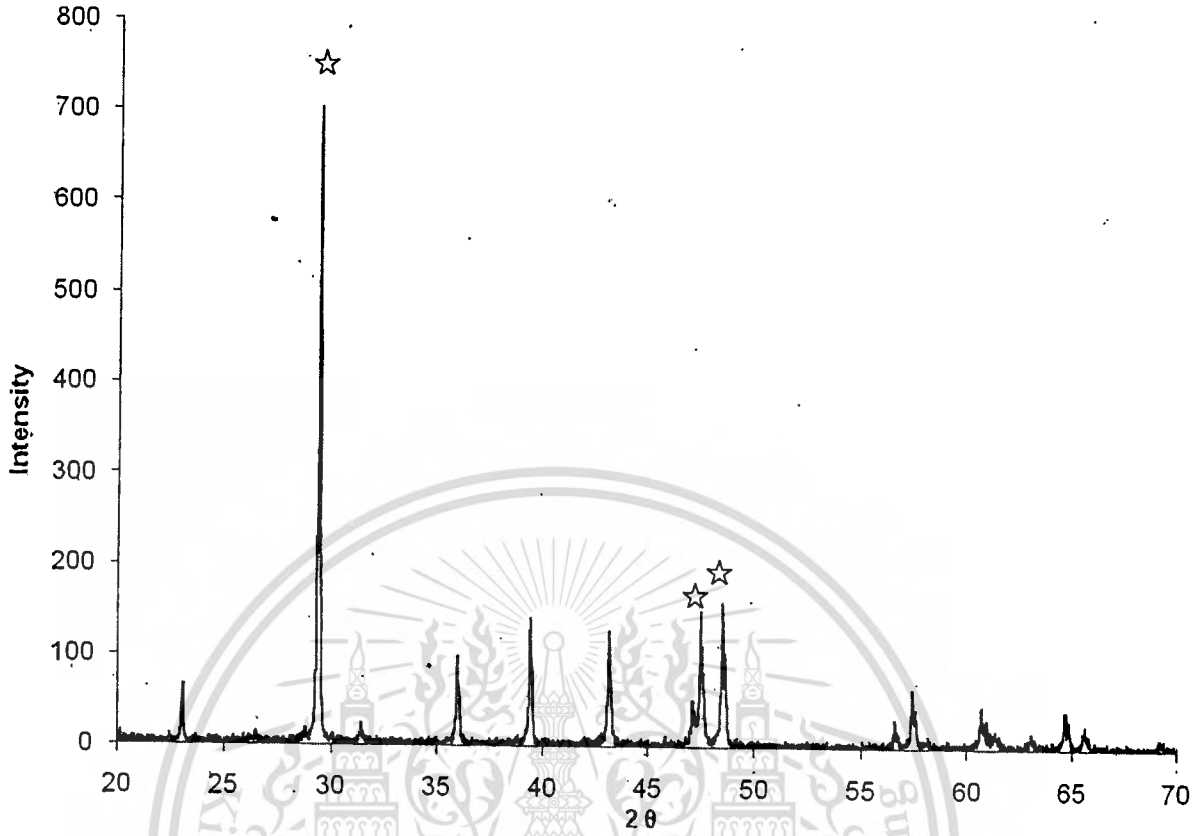


Figure 4.8: XRD pattern of PCC using $Ca(OH)_2$: 2.57 g / 2 L

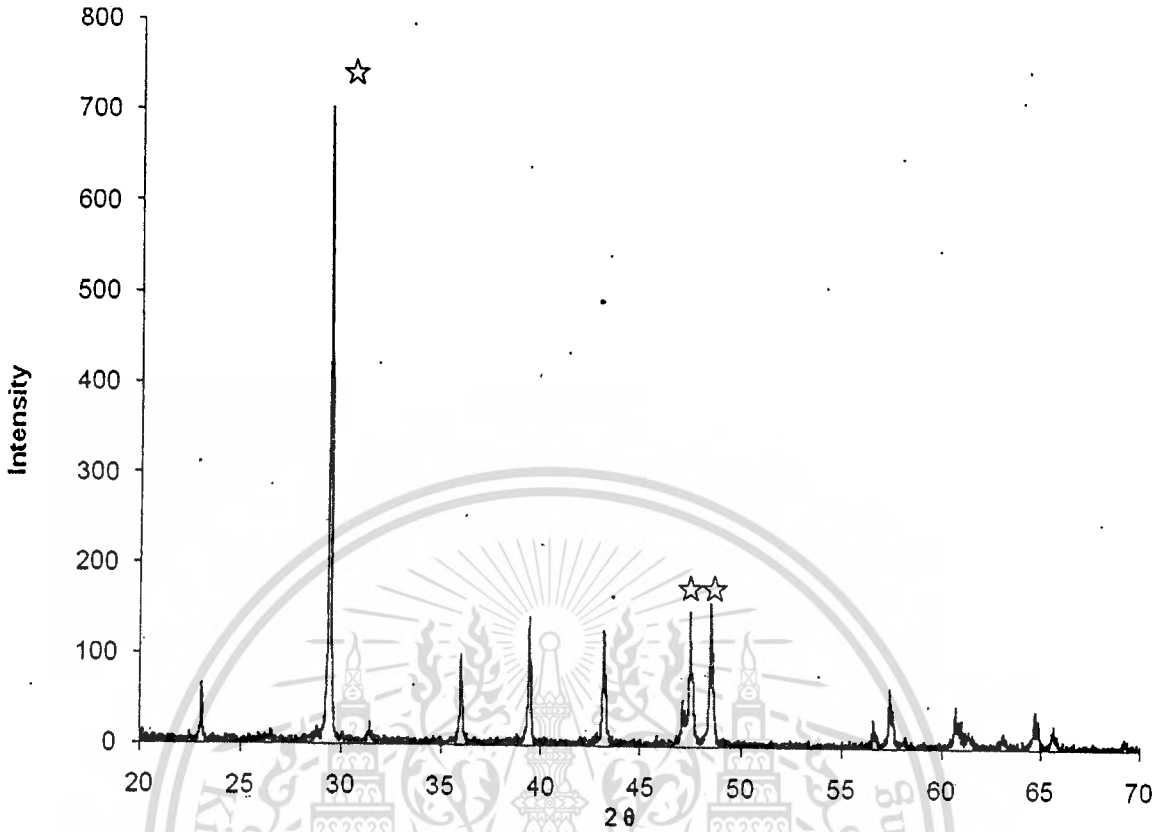


Figure 4.9: XRD pattern of PCC using $Ca(OH)_2$: 4.00 g / 2 L

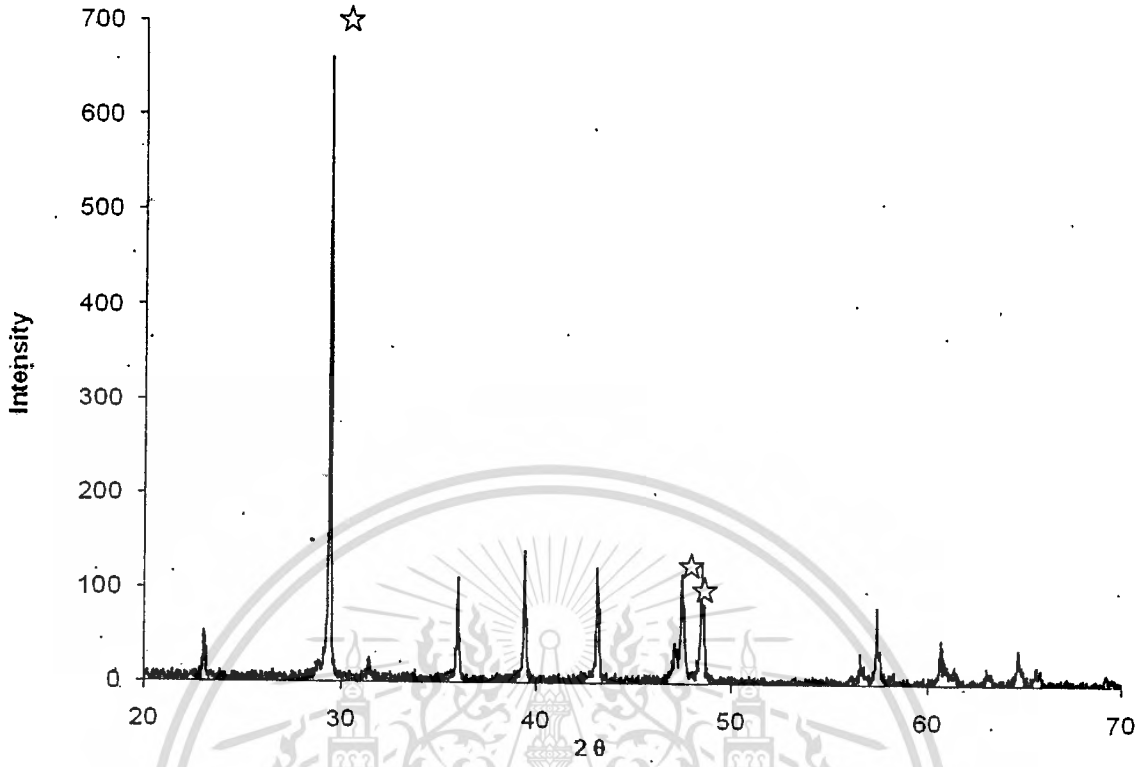


Figure 4.10: XRD pattern of PCC using $Ca(OH)_2$: 6.12 g / 2 L

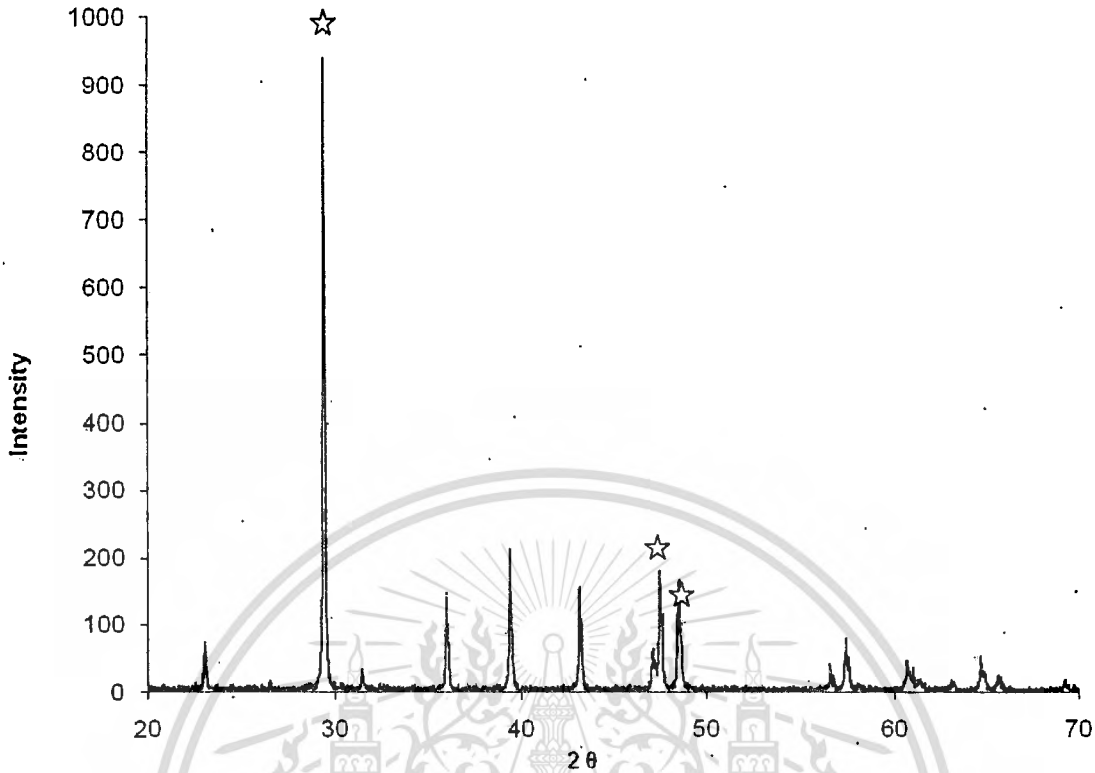


Figure 4.11: XRD pattern of PCC using $Ca(OH)_2$: 8.25 g / 2 L

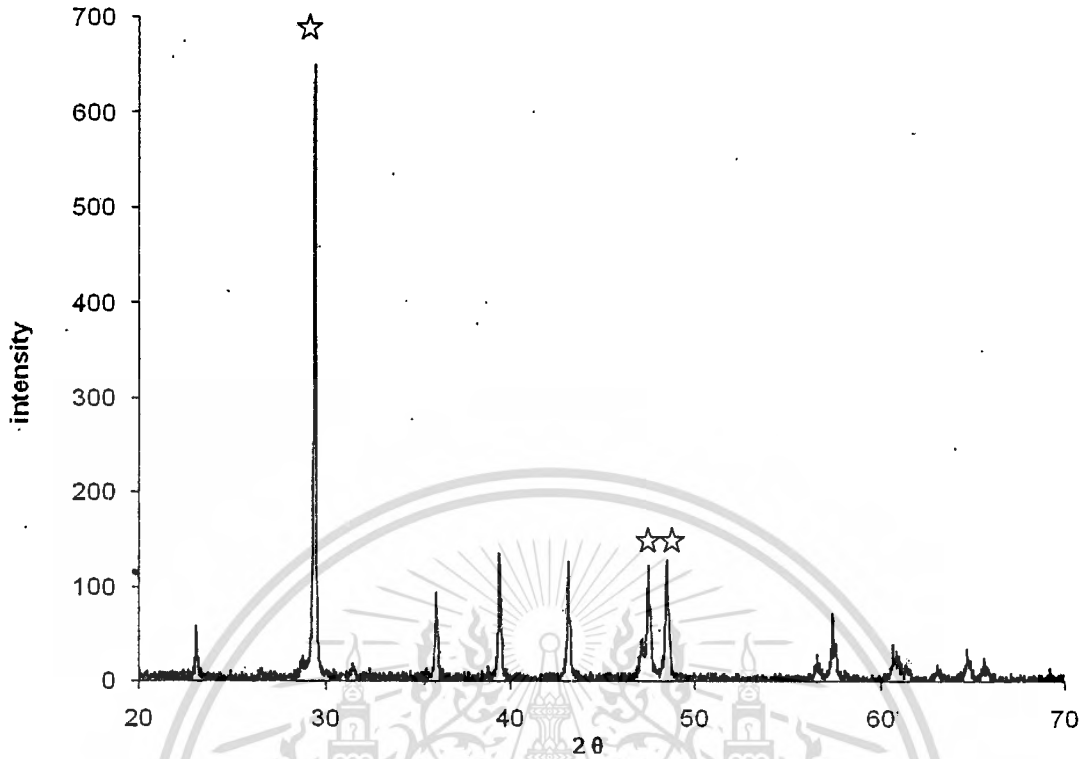


Figure 4.12: XRD pattern of PCC using $Ca(OH)_2$: 9.93 g / 2 L

Chapter 5

Conclusion and recommendation

5.1. Conclusion

This special project a high gravity rotating packed bed reactor, developed by Chen et al. was constructed and used to prepare NPCC. According to Chen et al., it was found that the prepared NPCC were calcite with cubic form. The obtained NPCC were 10 times larger.

5.2. Recommendation

For further study, HGRPB reactor should be in the horizontal way to prevent aqueous leak. Moreover, several factors that influence the particle size and morphology of NPCC should be investigated. These are the concentrations of calcium hydroxide, $Ca(OH)_2$, flow rate of carbon dioxide, rotating speed of RPB and reaction temperature.

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Appendices

Appendix A:

Reactor Set

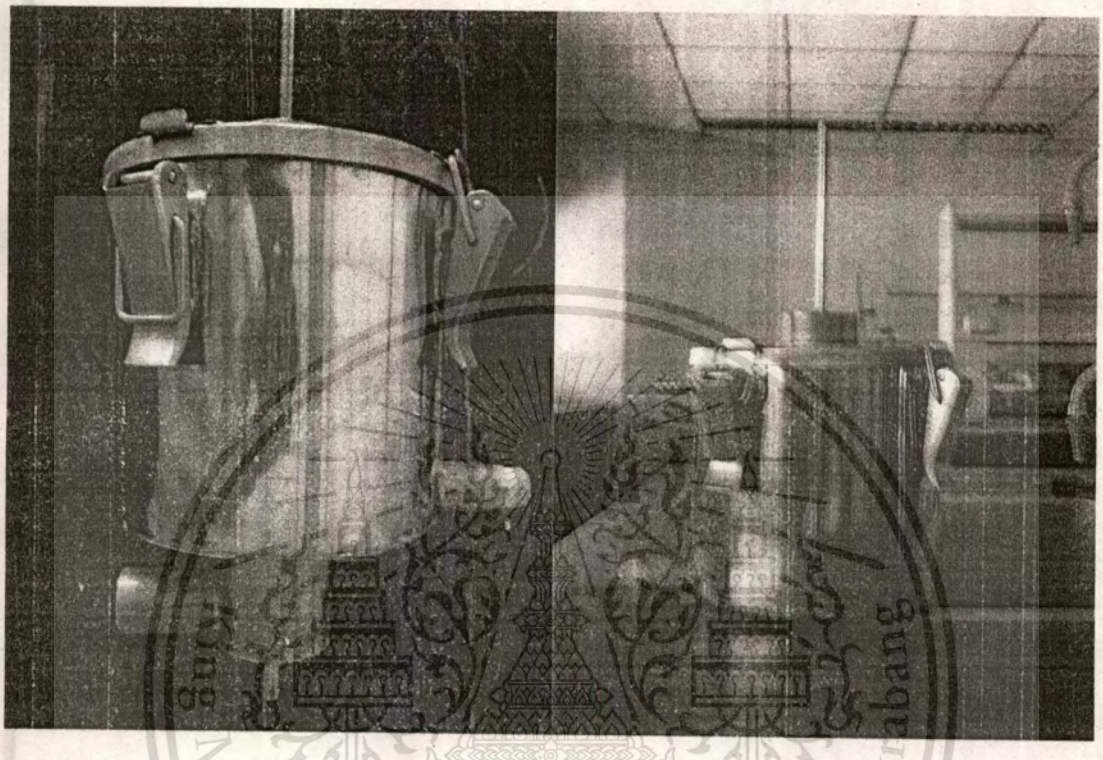

Figure 1: HGRPB Reactor

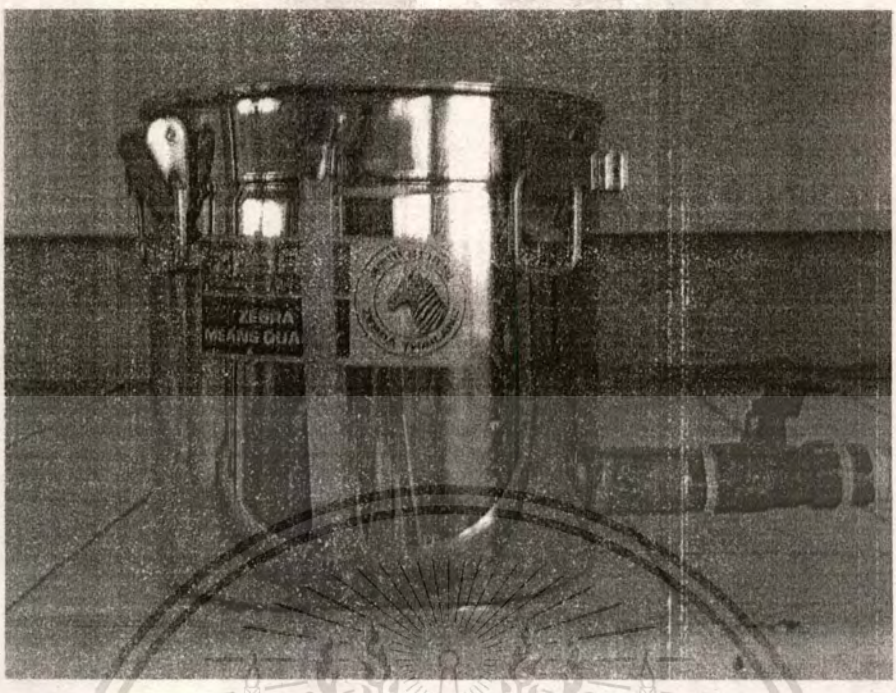

Figure 2: Feeding tank

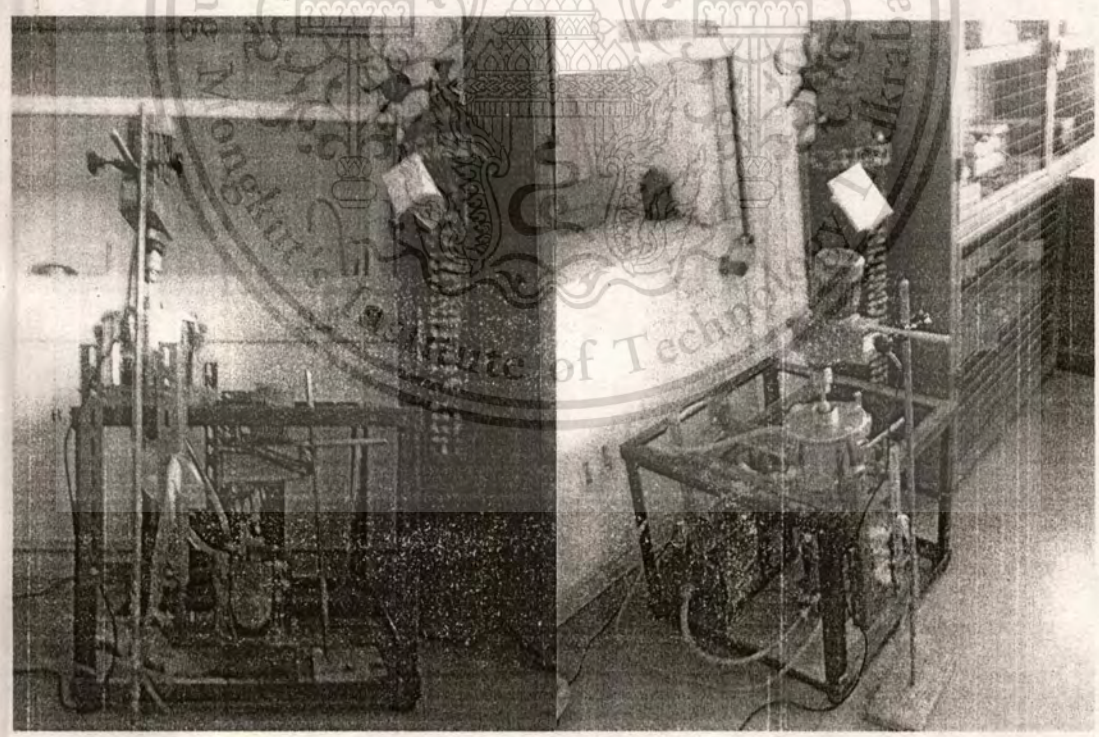

Figure 3: Experimental setup

Appendix B:

Experimental data

Table 1: HGRPB reactor test run

	Date	14/2/2009	Pressure (kg/cm^2):10					
				pH				
Sample	Wt: $Ca(OH)_2$ (g)	Wt: H_2O (g)	pH (intitial)	1st	2nd	3rd	4th	Temp. C
1	1.75	2040.42	10.180	5.610	5.630	5.670	5.680	27.8
2	2.57	2055.61	10.420	5.770	5.740	5.800	5.790	27.8
3	3.06	2042.34	11.320	5.860	5.870	5.880	5.871	27.6
4	4.00	1991.52	11.580	6.447	7.004	6.197	6.524	27.6
5	5.15	2034.91	11.647	6.770	6.525	6.031	6.106	27.6
6	6.12	2037.52	11.653	6.425	6.118	6.022	6.268	27.6
7	7.14	2031.09	11.729	6.476	6.440	6.057	6.061	27.6
8	8.25	2005.89	11.602	6.446	6.176	6.042	6.023	27.6
9	9.93	2152.17	12.150	6.160	6.050	6.050	6.050	27.6
10	11.06	2028.37	12.170	6.010	6.060	6.040	6.050	27.6