Synthesis of Precipitated Calcium Carbonate Nanoparticles Using Modified Emulsion Membranes

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Synthesis of Precipitated Calcium Carbonate Nanoparticles Using Modified Emulsion Membranes

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SUMMARY

The synthesis of precipitated calcium carbonate nanoparticles with the use of double water in oil emulsion has been developed. Restricting the mass of calcium ions present in the system makes it possible to predict particle size precipitated. A model was developed to calculate the concentration required to synthesize a desired particle size. This model took into account a coalescence factor. The coalescence factor is described at the probability of two emulsion droplets, with separate nucleation processes within them, colliding and forming one nucleation process. The Ca$^{2+}$ ions diffused through the oil membrane into the emulsion droplets with (CaCO$_3$)$^{2-}$ ions by concentration gradients and ‘facilitated transport.’ The size and shape of precipitated calcium carbonate synthesized was confirmed using scanning electron microscope and light scattering. Particles ranging from 100 nm to 1200 nm have been synthesized using mass restriction. The effect of temperature on the crystalline structure of precipitated calcium carbonate was studied. This was done by x-ray diffraction, where it was found that calcite was the dominating crystalline structure.
CHAPTER 1
INTRODUCTION

Nanotechnology is the creation of new materials, 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 nanostructures or nanoparticles are used in numerous technological and medical applications e.g. as ceramics, polymer composites, filler materials, pigments, electronics, catalysts, and many others [1]. Several techniques have been developed for such particles, some based on physical and some based on chemical principles. Using 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 1 μm is usually difficult, and can not be controlled easily
- The shape is irregular due to non-directed cracking
- Distribution is broad and uncontrolled

Therefore the need for wet chemical procedures is important. Wet chemical procedures have been found to be promising due to their low energy requirements and better control of particle size. Nanostructure can significantly change the properties of materials, such as optical properties, hardness, shape and morphology. For example, when conventional calcium carbonate is added to polypropylene it
forms agglomerates in the polymer matrix. However when nanometer sized CaCO$_3$
particles are used the polymer-particle interface area increases drastically and steric
hindrances are reduced. This can cause significant changes in the properties of the
composite.
CHAPTER 2
LITERATURE REVIEW

2.1 Precipitated Calcium Carbonate

Precipitated calcium carbonate (PCC) has been widely used as fillers for papermaking, coatings, plastics and agriculture. Its primary function in the paper industry is to reduce furnish costs and increase the brightness of paper, while still being inexpensive. The following are some main functions of PCC as a filler [2]:

- Improving printing quality by changing the smoothness, show through, ink absorption.
- Formation and sheet structure.
- Appearance properties.
- Dimensional stability.
- Texture and feel.

In the plastics industry it is used as a filler in polymer composites such as plasticized and rigid PVC, unsaturated polyesters, polypropylene and polyethylene [28]. In coatings, calcium carbonate is used as the main extender. The opacity of coatings is influenced by fineness and particle size distribution. Also, calcium carbonate enhances properties of the coating such as:

- Weather resistance.
- Anti-corrosion.
- Rheological properties.
- Low abrasiveness.
In water based coating calcium carbonate also reduces the drying time [28]. Calcium carbonate is also used in agriculture as a fertilizer. It is used to stabilize the pH of the soil. It is also used at times as a calcium supplement in animal feed stock.

However, currently used conventional PCC is 1-3 µm and nanosized PCC has not been used for papermaking. This study is to focus on the preparation of nano-sized precipitated calcium carbonate particles using a double emulsion liquid membrane and to explore its potential applications in both paper and non-paper related engineering materials.

PCC nanoparticles (<100 nm) have shown many unique properties compared to regular PCC particles (1-3 µm) [4]. Studies on the effects of precipitated calcium carbonate fillers in sealants and PVC materials have been made. It has been indicated that fatty acid-treated PCC of particle size less than 100 nm is particularly useful for filling sealants. Studies on the impact fracture energy of mineral-filled polypropylene and copolymer with and without calcium carbonate fillers showed that nanometer fillers increased the stiffness of both the homopolymer and copolymer [5].

Kovacevic et al. [6] 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 all [14] studied the application of CaCO₃
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 [7], 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 1 and 2 show some examples of SEM images of PCC particles of different morphology. Figure 1 shows spherical particles while figure 2 displays needle-like shape of the particles. These are not nanoparticles.

**Figure 1:** Spherical PCC

**Figure 2:** Needle-like PCC
2.2 Methods of Synthesis of Nanoparticles

There are various methods for the synthesis of nanoparticles. A nanophase material synthesized by gas evaporation is one of the methods [8], and was introduced by Granqvist and Burman. However, thermal evaporation is a known limitation to this method for metals and intermetallic compounds. This was later overcome by Hahn and Averback [9], 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.

Wang et al. [10] 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. [11] 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.

Liu et al. [13] prepared nanosized CaCO$_3$/SiO$_2$ composite particles by the sol-gel process of CaCO$_3$ and Na$_2$SiO$_3$ 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, [14]. Zhang et al. [15] synthesized nanoparticles of calcium carbonate in the reaction system of Ca(OH)$_2$-H$_2$O-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.

2.3 Liquid Emulsion Membrane (LEM)

Liquid emulsion membranes were first developed by Li at Exxon [3]. Bubble or liquid emulsion membranes first received a great deal of attention in the 1970s and 1980s. LEM have a large number of applications in removal and recovery of metals from large, dilute solutions. In recent times, this method has been used for the synthesis of nanoparticles and macromolecular size particles. The use of internal phase to control particle size and morphology has been a recent point of interest.

The process consists of four main steps. The first step is mixing the aqueous internal phase with an organic phase to form a liquid/oil emulsion. It is then further mixed in a larger mixing vessel with an external aqueous phase to form a water/oil/water
emulsion. The external phase contains the ions that will be transported across the membrane to react with the internal phase. A typical illustration of the process involved in LEM can be seen in Figure 3 below.

Figure 3: Schematic of Liquid Emulsion Membrane Process

The transport of metal ions occurs via facilitated transport using carriers and concentration gradients from the feed solution though the walls of the emulsion into the product solution. This occurs in the third phase. Here the metal ions form precipitates which can then later be removed as product after the solution has been demulsified. The minute emulsion droplets are commonly referred to as micro reactors. The micro sized internal emulsion droplets are considered as separate reactors such that the control of particle size is independent of the overall solution conditions but that within the emulsion droplet.

One of the advantages of using LEM is that it can be designed to be highly selective depending on the purpose required [7], for example in the removal of lithium from a potassium and sodium mixture. 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, [7] reported that LEM can be used to synthesize spherical calcium phosphate particles.

The optimal operating conditions for such systems vary from process to process. Factors such as ion concentration in both phases, pH and temperature play a large role in the product properties. The emulsion concentration will be varied to produce different PCC products. One disadvantage of LEM is the emulsion becomes unstable after prolonged contact with the feed solution and high speed mixing. The effects of such variables will also be analyzed for the scope of this project. The main objective of this study is to develop a system to synthesize precipitated calcium carbonate particles with controlled particle size in the range of nanometers, by the use of modified emulsion liquid membranes.

2.4 Liquid Emulsion Membranes in Industry:

Liquid membranes overcome the problem that most membranes have shown [16] of low specific transport rates. Liquid membranes are homogenous, non-porous membranes. A solute is dissolved at one side of the membrane and released to the other side by the concentration difference between the interfaces being the driving force. The addition of a carrier (or extractant) is used to enhance the transportation rates of ions across the membrane. The carrier reacts with the solute and the mass transfer is accelerated. This is known as ‘facilitated transport.’ Coupled transport is also an important phenomenon in the extraction of metals, where the carrier also reacts with an auxiliary component as well as the solute, thus maintaining a high concentration difference for long periods of time.
The surfactant and diluent are two important components of the emulsion liquid membrane. Generally aliphatic diluents have been used because of the lower solubility in water for example oil and kerosene. The surfactant determines the stability of the emulsion and controls various properties, some of which are, solubility in water, osmosis and mass transfer resistance.

The profitability of an emulsion liquid membrane depends on various parameters; therefore it is calculated for only specific problems [16]. The lower investment costs in liquid membrane permeation are due to the smaller sizes of equipment used. Various mass transfer mechanisms also affect the profitability of the system. Generally less organic extractant input can be a considerable factor in the economy of the process.

2.5 Synthesis of PCC Nanoparticles with the use of modified emulsion membrane

A typical LEM consists of three phases, the internal phase (water), and external phase (water), and an oil phase [W1/O/W2]. The LEM displayed tendencies to become unstable with high mixing and longer reaction times. High speed mixing caused the external water layer [W2] to break up and form water in oil emulsions [W2/O]. Water from the external phase would become part of the internal phase droplets, therefore diluting the concentrations. This caused errors in predictions and made control of particle size inaccurate. The method chosen was modified to have two separate water/oil emulsions. This overcame the problem of an unstable external phase. All other factors remained the same. This also allowed the droplets of carbonate ions to interact within the system freely therefore having a more uniform concentration gradient in all droplets.
However in LEM systems, the droplets with carbonate ions are limited to having higher concentration gradients closer to the outer circumference of the oil droplet. This is illustrated in Figure 4 and Figure 5 below.

**Figure 4:** Illustrates the effect of LEM on possible concentration gradient irregularities

**Figure 5:** Emulsion droplets in current method used; droplets are free to move within the system, therefore having a more uniform concentration gradient.

The first step is forming Emulsion A i.e. the formation of a W/O emulsion system with carbonate ions in the aqueous phase. Carbonate ions dissolved in water, are emulsified in kerosene which has a dissolved carrier. A second emulsion is made with calcium ions dissolved in water, and emulsified in the same kerosene phase. This is called Emulsion
B. Equal volumes of A and B are mixed and the reaction is allowed to occur with constant agitation to keep the emulsion stable. Once the reaction is completed, the agitation is terminated, and the emulsion demulsified using ethylene glycol to collect the precipitate. Details of the method used can be found in section 3.1.1.

The ions will permeate from the emulsion B droplets into the emulsion A droplets across the oil membrane as seen in Figure 7. There are two types of metal permeation: one where simple diffusion occurs due to the concentration gradient present across the phases. The second type consists of permeation by adding oil-soluble but water-insoluble carrier into the oil phase. This is more effective. The precipitate formed is collected for characterization.

2.6 Influencing LEM Parameters

2.6.1 Carrier Mechanism:
The transport of calcium ions through kerosene membrane is an integral part of the ‘facilitated transport’ to form precipitated calcium carbonate. D2EHPA [Bis(2-ethylhexyl) hydrogen phosphate] is a widely used extractant. The molecular structure of D2EHPA can be seen in Figure 6. The rate of extraction has been found to be dependent on the concentration gradient across the membrane, temperature and pH [18]. It has been seen from similar studies that a lower pH and lower concentration in the internal phase promotes ion transfer across the membrane.
At stage I, carrier A forms an oil soluble complex with Ca\(^{2+}\) ions as shown in the equation below.

\[
\text{Ca}^{2+} + 2\text{HA} \rightarrow \text{CaA}_2 + 2\text{H}^+
\]

Due to its high solubility in oil, this complex then penetrates through the oil membrane much more easily from emulsion B droplets to emulsion A droplets. Here it reacts with the CO\(_3^{2-}\) to form CaCO\(_3\) particles with the release of the carrier in the equation below:

\[
\text{CaA}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{CaCO}_3\downarrow + 2\text{HA} + 2\text{OH}^-
\]

The remaining carrier picks up a H\(^{+}\) from the aqueous phase to form a neutral carrier, then diffuses back through the oil membrane to the external surface and reacts with Ca\(^{2+}\) to form more complexes. This continues until all the calcium ions have been reacted with the CO\(_3^{2-}\) and the reaction can not go any further. It should be noted that sodium salts do not tend to form a complex with the carrier as they are insoluble in the organic phase. The absorption of H\(^{+}\) is more stable and therefore more likely to occur. Figure 7 shows the overall mechanism involved.
2.6.2 Emulsion Properties:

During the transport process, the emulsion drop will undergo changes in shape. There are two main changes that may occur, a particle may collide and agglomerate and form larger droplets, the second is the particles may break and form smaller droplets due to shear forces present from agitation. By increasing the surfactant concentration it is possible to increase the stability of emulsions. Generally the emulsion droplet diameter can vary between 0.5 and 10 µm.

The mass transfer is diffusion controlled and can be modeled after Fick’s first law of diffusion, as can be seen in Figure 8. Thus the viscosity of the diluent plays an important role. However, the mass transfer also is enhanced by adding a carrier to the organic solution. For the purpose of this study, the rate at which the calcium ions are transported across the organic membrane has been taken as the limiting step. The reaction between
calcium ions and carbonate ions has been assumed instantaneous in comparison to transport rates.

![Diagram](image)

**Figure 8**: Concentration gradient for mass transfer.

### 2.6.3 Surfactant Selection:

Hydrophile – Lipohile Balance also known as HLB was a method proposed by Griffin, as a guide to select an optimal emulsifying agent [20]. It has been shown by Sherman that HLB depends on both concentration as well as phase volumes of the oil and water.

HLB is used to characterize most oil phases using solubility parameter (SP) values. The higher the HLB the higher the solubility in water. The SP values may also be derived from basic physical properties [21]. The HLB value is derived from the following equation:

\[
HLB = 4 \left( \frac{SP + 7}{8} \right)
\]
This equation is used to predict the stability of emulsions and select optimal emulsifying agents. Therefore, generally, a lower HLB number is used for water in oil (W/O) emulsifications and a higher HLB number is used for oil in water (O/W) emulsifications. For this study SPAN – 83 (Aldrich) was used with the molecular structure shown in Figure 9, with HLB value of 3.

\[
R = \left( \text{CH}_2 \text{CH} = \text{CHCH}_2 \text{CH}_2 \text{CH}_3 \right)_{15}
\]

**Figure 9:** Molecular Structure of Span – 83, Sorbitan Sesquioleate

**2.6.4 Solubility of Membrane Phase:**

The solubility of the membrane is of great importance [16]. The solubility range varies from 3 – 8 ppm carbon. Some factors that affect the solubility are the components used, the pH of the aqueous phases and the concentrations of the inert salt. Also the surfactant added can affect the solubility and must be chosen to be compatible with the system being used. Usually aromatic diluents are preferred because of the lower solubility in water and higher emulsion stability.
2.6.5 Preparation parameters on Internal Drop size:

The size and size distributions of emulsion droplets are factors that affect the physical and qualitative stability of emulsions. Also size and size distribution are factors that affect chemical reactivity, rheology and physiological efficiency [19].

Characterizations of emulsions can be done by measurement of surface area. The size of the droplets in the emulsion is measured using an optical microscope [17]. Droplets less than 1 µm are difficult to measure using the microscope. The internal drop size affects mass transfer rate. The speed of rotation, time and weight percent, are three main factors that affect the droplet size when forming emulsions. The higher the speed and time, the greater the surface area [17], since the droplet size is much smaller under these conditions. Emulsions with higher surface area show in general to have an increased mass transport, compared to those with lower surface area [17].

2.7 Polymorphism of PCC

Precipitated calcium carbonate has been reported to usually be in three basic form: calcite, vaterite and aragonite, where calcite is the most thermodynamically stable and vaterite the least under ambient conditions. Table 1 shows the general availability of calcium carbonate crystals [22].
Table 1: Availability of calcium carbonate crystals

<table>
<thead>
<tr>
<th></th>
<th>Biological</th>
<th>Non-biological</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite (C)</td>
<td>very common</td>
<td>very common</td>
</tr>
<tr>
<td>Aragonite (A)</td>
<td>very common</td>
<td>rare</td>
</tr>
<tr>
<td>Vaterite (V)</td>
<td>rare</td>
<td>very rare</td>
</tr>
<tr>
<td>Non-crystalline CaCO₃</td>
<td>rare</td>
<td>non-existent</td>
</tr>
</tbody>
</table>

Yamaguchi et al. [27] found that vaterite forms calcite crystals over several hours, and aragonite forms calcite over a period of several months at room temperature. Higher temperatures accelerate the transformation. Wray and Daniels [26] found that when precipitated calcium carbonate is formed from highly saturated aqueous solutions, aragonite is predominately formed at 70 °C and vaterite is formed at 30 °C [23].

Ogino et al. [23] proposed that during calcium carbonate formation in water, the mechanism involved first the formation in an amorphous unstable form of calcium carbonate which within seconds converted into the crystalline structure. Various inhibitors can affect the crystalline formation mechanism such as surfactant, or presence of composites and contaminants.

Studies have been conducted by Ogino et al [23] to study the shape change of the crystals formed during formation of precipitated calcium carbonate in water. Calcite has been reported to take on the form of a rhombohedral shape, while aragonite has shown both octagonal and needle like structures. Vaterite has shown to form hexagonal crystal structures. Ogino also reported that once the particles had been formed and were
subjected to heat, the calcium carbonate crystals transformed into the more stable calcite form. X-ray diffraction is used to determine crystalline structure. Figure 10 shows the comparison of XRD peaks from the database for all three crystalline structures present in calcium carbonate.

![XRD Data for calcite, aragonite and vaterite](image)

**Figure 10:** XRD Data for calcite, aragonite and vaterite

### 2.8 Dispersion Mechanisms:

It has been found that agglomerates of the nanoparticles tend to form after synthesis which may cause erroneous data. Dispersion is the process of breaking apart large agglomerates and ensuring wetting of the particle surface, to ensure particle separation [24]. Dispersants are used to maintain particle separation by steric hindrance or electrostatic stability. A commonly used chemical dispersant is Triton X – 100 (octylphenol ethylene oxide condensate).
Ultrasonic agitation is a common method used to disperse agglomerates. The duration, acoustic power and temperature affect the extent of agglomeration. It has been found that short durations of 1 – 3 minutes are sufficient to form a well dispersed suspension. Once the agglomerates have been broken up by ultrasound, this allows the Triton-X 100 to adhere to the surface of the particles and prevent further agglomeration.
The objective of this part of the study was to synthesize precipitated calcium carbonate of various sizes using the calcium ion concentration as the control. The data was plotted to obtain a relationship for ion concentration with particle size and was compared to the theoretical number predicted mathematically. The results were repeated at higher temperatures to study the effect of temperature on particle size, morphology and emulsion stability.

3.1 Synthesis of PCC using emulsion membranes

3.1.1 Emulsion Preparation:
The experimental procedure used was modeled after the procedure used by Takayuki Hirai et al. [7]. Hirai used a LEM system. However, as mentioned before, the water/oil/water emulsions tended to become unstable with time, and at high speed mixing caused the external water layer to break up and become emulsified. A double emulsion membrane method has been proposed.

The system contained two separate water and oil emulsions. Both emulsions involved forming an emulsion of equal volume of an aqueous phase and an organic phase. The concentrations of all phases are shown in Table 2 below.
Table 2: Concentrations of all phases

<table>
<thead>
<tr>
<th>Emulsion A: Aqueous Phase</th>
<th></th>
<th>Emulsion A: Organic Phase</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Concentration in Water</td>
<td>Chemical</td>
<td>Concentration in Kerosene</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>0.1 M</td>
<td>Bis(2-ethylhexyl) hydrogen phosphate</td>
<td>0.06 M, 6 % by wt</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>0.2 M</td>
<td>Span- 83</td>
<td>0.12 M</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>0.18 M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>Emulsion B: Aqueous Phase</th>
<th></th>
<th>Emulsion: Organic Phase</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Concentration in Water</td>
<td>Chemical</td>
<td>Concentration in Kerosene</td>
</tr>
<tr>
<td>Calcium Nitrate</td>
<td>Calculated to control size</td>
<td>Bis(2-ethylhexyl) hydrogen phosphate</td>
<td>0.06 M, 6 % by weight</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Span- 83</td>
<td>0.12 M</td>
</tr>
</tbody>
</table>

Bis(2-ethylhexyl) hydrogen phosphate (D2EHPA) was used as the carrier and Span 83 (sorbitan sesquioleate) was used as a surfactant. The HLB number for Span 83 is 3. The surfactant determines the stability of the emulsion. Sodium hydroxide was added to
maintain a lower pH as this creates a more feasible condition for the formation of precipitated calcium carbonate. Sodium nitrate was added to maintain conductivity in the system as the free ion concentration is changing as reaction occurs.

Equal quantities by volume of the aqueous phase and organic phase were taken and emulsified using a high shear mixer. The droplet size of the emulsions was measured using optical microscope. Some parameters that affect the droplet size are speed of the homogenizer, time of emulsification, viscosity and aqueous weight loading. Finally equal volumes of emulsion A and emulsion B were mixed and stirred at 300 rpm using an impeller stirrer. Figure 11 shows a schematic of the process involved in preparing the emulsion.

![Figure 11: Schematic of emulsion preparation procedure](image)

The system was allowed to react for 30 minutes, where it has been assumed that complete reaction has occurred, based on a study conducted by Qunhui Sun and Yulin Deng [25]. Transport rate of the ions depend on the carrier, concentration and temperature. Sun et al. conducted a study to measure the calcium ion concentration in the external phase of an
LEM system with D2EHPA as the carrier. The test was conducted at room temperature. These conditions mimicked the conditions used for the study. It was reported that within the first 15 minutes 80% of the calcium ions had diffused through the membrane, and by 30 minutes there were no detectable calcium ions left.

3.1.2 Demulsification and Particle Collection

After 30 minutes under constant agitation at 300 rpm, the system was demulsified by adding 15% by weight ethylene glycol to the emulsion mixture. This was then centrifuged at 5000 rpm for 30 minutes in Beckman, J2-HC centrifuge. Two distinct phases were formed as can be seen in Figure 12, a heavy aqueous phase and a light organic phase. The particles were found to be present predominately in the interface of the two phases. Some of the larger particles tended to settle to the bottom of the aqueous phase. It was seen during earlier experiments that the smaller PCC particles were difficult to collect. Therefore the centrifuged system was allowed to stand overnight to allow the particles to agglomerate and centrifuged again at 5000 rpm for 30 minutes. The particles were then large enough to be seen and the interface was removed and washed in excess ethanol. The resulting solution was centrifuged again, and it was found that the particles settled to the bottom of the container. The PCC was washed with ethanol two to three times and then washed again in water two to three to remove any remaining hydroxide, nitrate and sodium ions.
Figure 12: Phase Separation of the emulsion after centrifuge

The final PCC particles obtained were dispersed in water solution with 0.05% *triton-X 100* by volume. The solution was then exposed to high ultrasound waves using the *W-385 Sonicator* for 1 minute at 15% output power, to completely break any remaining agglomerates. This solution was ready for particle characterization.

The concentration of calcium ions in Emulsion B was used as the control, to predict particle size with the assumption of complete reaction. The above method was repeated for various calcium ion concentrations and the particle size was calculated for each test. A calibration curve was developed to determine the relationship between the particle size and calcium ion concentration.

The above test was repeated for higher temperatures to study the effect of temperature on emulsion stability and particle size. The two emulsions were reproduced at various concentrations. Equal volumes of emulsion A and emulsion B were mixed and
constantly agitated at 300 rpm for 30 minutes. The solution was placed in a hot water bath at a constant temperature of 60 °C.

3.1.3 Particle Size Prediction

The calcium ion concentration was adjusted to suit the test purpose and was calculated based on the assumption that only one nucleation site occurs per droplet of aqueous solution. Since each droplet will be treated as a ‘micro-reactor’, particle size or rate of reaction can be controlled by changing concentration gradients across the emulsion membrane. For the purposes of this study it was assumed that the reaction has occurred to completion. The following equations describe the method used to predict the calcium ion concentrations required to give a specified particle size.

\[
\text{Weight of droplet in aqueous phase A} = \frac{4}{3} \pi r_1^3 \rho_{\text{water}},
\]

Where: \( r_1 \) = radius of emulsion droplet, 1.5 \( \mu \text{m} \),
\( \rho_{\text{water}} \) = Density of water, 1 g/cm\(^3\).

\[
\text{Number of droplets in aqueous phase A} = \frac{\text{Weight of aqueous phase A}}{\text{weight of droplet}}
\]

\[
\text{Weight of CaCO}_3 \text{ Particle} = \frac{4}{3} \pi r_2^3 \rho_{\text{CaCO}_3},
\]

Where: \( r_2 \) = radius of CaCO\(_3\) nano-particle to be synthesized,
\( \rho_{\text{CaCO}_3} \) = density of CaCO\(_3\), 2.93 g/cm\(^3\).

Total weight of CaCO\(_3\) = weight of CaCO\(_3\) particle x Number of droplets.

This is based on the assumption that every droplet contains one PCC particle and the density for water remains constant.
Concentration of aqueous phase B = \frac{\text{total weight of CaCO}_3}{\text{MW CaCO}_3 \times \text{Vol of aqueous Phase B (ltrs)}}, \quad (5)

Where: \quad \text{MW CaCO}_3 = \text{Molecular Weight of CaCO}_3.

It was found later that the particles synthesized were larger than the modeled size due to coalescence of the emulsion droplets, causing fewer particles to be formed, while having a larger diameter. A correction factor was incorporated into the model to attempt to increase accuracy of the theoretical numbers. This correction factor assumes that various percentages of droplets collided to form agglomerates, therefore reducing the number of particles by that percentage. The number of droplets that agglomerate was then assumed to have twice the droplet diameter. Details of the mathematical equations used can be seen as follows.

An agglomeration percentage was assumed. This meant that a certain percentage of droplets in the 100 ml system agglomerated, causing the number of particles in the system to reduce by that percentage. Based on this assumption, new concentration vs. particle size was calculated.

Assume x\% collision, and basis of 100 ml Emulsion A.

Volume with droplet diameter \( r_1 \) \( (V_1) = (1-x) \times 100 \) \hspace{1cm} (1)

Volume with droplet diameter \( 2r_1 \) \( (V_2) = x \times 100 \) \hspace{1cm} (2)

Where: \quad r_1 = \text{radius of emulsion droplet, 1.5 \mu m}

\( \rho_{water} = \text{Density of water, 1 g/cm}^3 \)
Weight of droplet of radius \( r_1 \) (\( W_1 \)) = \( \frac{4}{3} \pi r_1^3 \rho_{\text{water}} \) \hspace{1cm} (3)

Number of droplets with radius \( r_1 \) (\( N_1 \)) = \( \frac{V_1}{W_1} \) \hspace{1cm} (4)

Weight of droplet of radius \( r_1 \) (\( W_2 \)) = \( \frac{4}{3} \pi (2r_1)^3 \rho_{\text{water}} \) \hspace{1cm} (5)

Number of droplets with radius \( r_1 \) (\( N_2 \)) = \( \frac{V_2}{W_2} \) \hspace{1cm} (6)

Total Number of Droplets (\( N \)) = \( N_1 + N_2 \) \hspace{1cm} (7)

Weight of CaCO\(_3\) Particle = \( \frac{4}{3} \pi r_2^3 \rho_{\text{CaCO}_3} \) \hspace{1cm} (8)

Where: \( r_2 \) = radius of CaCO\(_3\) nano-particle to be synthesized
\( \rho_{\text{CaCO}_3} \) = density of CaCO\(_3\), 2.93 g/cm\(^3\)

Total weight of CaCO\(_3\) = weight of CaCO\(_3\) particle \( \times \) Number of droplets (\( N \)) \hspace{1cm} (9)

This is based on the assumption that every droplet contains one PCC particle.

\[ \text{Conc of aqueous phase B (new)} = \frac{\text{total weight of CaCO}_3}{\text{MW}_{\text{CaCO}_3} \times \text{Vol of aqueous Phase B (ltrs)}} \] \hspace{1cm} (10)

Where: \( \text{MW}_{\text{CaCO}_3} \) = Molecular Weight of CaCO\(_3\)

### 3.2 Characterization of Particles

The objective of this part of the experimental was to determine an effective method to measure the size of the particles synthesized and to obtain a clear image of the shape of
particles. The following equipment was used to study the particles size during the test work.

3.2.1 Light scattering particle size analyzer

Particle size was measured using Malvern 3000 Zetasizer in size mode. The software used was Zetasizer 3000, PCS version 1.32a. The synthesized PCC was dispersed in water with 0.05% triton by volume to form a stable suspension. The light scattering was conducted at various concentrations at 25 °C.

3.2.2 SEM (Scanning Electron microscopy)

The scanning electron microscope used was model JSM 6400 by Jeol. The SEM samples were prepared by placing a drop of the dispersed PCC on carbon tape and oven dried around 65 °C. The two sided carbon tape was then mounted onto aluminum stubs and gold plated using the Hummer V sputter coater for 3 minutes. For smaller particles it appeared that the irregularities on the carbon tape surface caused interference with the image, making it difficult to focus on the particles. To reduce the interference a glass cover was placed over the carbon tape. The dispersed PCC solution drop was then placed on the glass cover slip and oven dried before gold plating. Images were obtained using the dpict 32 – Digital Photo Image Collection Tool, version 2.310, by Geller Micro-analytical Lab. The images were used to measure the size of 20 random particles and the average was taken as the particle size.
3.3 XRD Study

Ogino et al [23] reported that calcium carbonate when synthesized at higher temperatures in highly supersaturated solutions with calcium and carbonate ions, displayed polymorphic characteristics. The XRD study was to determine if this was applicable for emulsion membranes at higher temperatures. Large amounts of PCC particles were synthesized at four conditions as shown below.

1. 600 nm particles reacted for 30 minutes at 60 °C
2. 200 nm particles reacted for 30 minutes at 60 °C
3. 600 nm particles reacted for 30 minutes at room temperature
4. 200 nm particles reacted for 30 minutes at room temperature

The particle sizes given above are the predicted sizes and may vary from actual synthesized sizes. The samples were washed with water to remove any unwanted sodium, hydroxide, and nitrate ions. This was then dried in the oven to form a white powder. The samples were placed on a low background powder specimen holder and analyzed using x-ray diffraction, which used APD 3720 control system and XRG 3100 x-ray generator manufactured by Philips. The program used to measure the peaks was PCAPD, version 3.6, and the peaks were identified and catalogued using PW 1876 PC-Identify, version 1.0 and PCPDFWIN, version 1.2 respectively. A step size of 0.01° of 2theta was taken at 0.01°2theta/second at 10° to 70°.
3.4 Emulsion Stability Study

There are various parameters that affect the size of the emulsion droplets. The particle size calculations are dependent on the emulsion droplet size. The droplet size was measured using an optical microscope, *LEICA DMLM*. Samples were removed from the bulk emulsion at various time intervals and placed on a glass slide. Digital pictures of the emulsion were taken at 500 times magnification using *LEICA IM50, version 1.2* and *UTHSCSA Image Tool, version 3.0* software was used to measure the size of the droplets. The data reported was the average size of 40 random droplets.

Three conditions were studied. The first one was a stability study of the final mixture of emulsion A and emulsion B at a 1:1 ratio by volume. Constant agitation at 300 rpm for 30 minutes was applied to the emulsion to maintain the same reaction conditions as all the synthesis had been conducted. Samples were collected around every 10 minutes for half an hour. The final two studies were of Emulsion A and Emulsion B without the presence of any agitation. Samples for these two studies were collected at 10 minute intervals for one hour.

3.5 Partial Volume Study

The objective of this part of the study is an attempt to evaluate the nucleation mechanism of the ions, and study crystal formation. The test was to evaluate the effect of limited droplets containing calcium ions on particle size. The aim was to see if the ions tended to nucleate within a certain area of carbonate ions and form larger particles or evenly disperse throughout the emulsion. This study involved taking 200 ml of emulsion B, and adding 25 ml of emulsion A. The calcium concentration in this emulsion was calculated
to give a particle size of 450 nm if equal volumes of emulsion A and B were used. The system was allowed to react for 30 minutes, and samples were removed for analysis. Another 25 ml of Emulsion A with the same calcium concentration was added and allowed to react for 30 minutes and samples removed for analysis. This was repeated until a total of 100 ml of emulsion A had been added to the system and a period of two hours had elapsed. Figure 13 shows the schematic of the overall process involved. The samples were demulsified and washed. The particles collected were analyzed using SEM and light scattering.

**Figure 13:** Schematic of Partial Volume Study
CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 Particle size relationship with concentration:

Figure 14: Relationship of concentration of calcium ions with particle size, synthesized at room temperature

In Figure 14 the particle size measured using SEM and light scattering increased with concentration as predicted, where the error bars were calculated with a 90% confidence interval. The results obtained from SEM correlated well with results obtained from light scattering. The sizes of the particles measured however were larger than those predicted using the mathematical model without the correction factor. The mathematical model was based on the assumption that only one particle exists within each emulsion droplet, whereas in fact, the droplets are constantly colliding with each other, joining to form one large droplet and then breaking apart again. During this process it may be possible for...
the two particles to remain within a droplet, while the second droplet would not have any particle present within it. This collision of droplets may cause the actual size of the particle synthesized to be larger than those predicted. Also the difference between light scattering data and SEM may be attributed to the presence of some agglomeration and the hydrodynamic effect.

Figure 15 shows the trends obtained from the model using the correction factor. Various percentages of coalescence were assumed and the model plotted to obtain a comparison with actual synthesized data. It can be seen that the assumption of 70 – 80% dimerization between the particles fit the data most accurately.

![Figure 15: Relationship of concentration of calcium ions with particle size, synthesized at room temperature, with correction factor in model.](image-url)
The same can be seen with Figure 16 when the particles were synthesized at higher temperatures. Various parameters change with change in temperature. Increasing the temperature affects diffusion rates and viscosity. At higher temperatures the rate of diffusion is faster and the viscosity of the oil and water phase is lower. This means that the emulsion droplets would be more likely to agglomerate and form large particles as can be seen in Figure 16. Also the surface tensions of most liquids reduce with increase in temperature. This affects the surfactant adsorption at the interface and changes the emulsion stability.

**Figure 16:** Relationship of concentration of calcium ions with particle size, synthesized at 60 °C.
The SEM images obtained, gave insight into the shape of the precipitated calcium carbonate. Figure 17 below show particles that were synthesized at 60 °C and were modeled to be 600 nm in size. The actual size of the particles was found to be 1115 nm. Figure 18 shows another example of the SEM images obtained. The samples were synthesized at room temperature and calculated to be 450 nm using the mathematical model. The actual measured size was 467.5 nm. SEM images of all samples can be found in Appendix A.

**Figure 17**: SEM image of 1115 nm PCC, synthesized at 60 °C

**Figure 18**: SEM image of 467.5 nm PCC synthesized at room temperature

### 4.2 XRD Study

Figure 19 shows the x-ray diffraction results obtained. It can be seen from Figure 19 that the crystalline structure of the precipitated calcium carbonate at all four conditions is the same. From the *PW 1876 PC-Identify, version 1.0* software used to identify the type of crystalline structure, it was found to be predominantly calcite.
Figure 19: 2 theta values for peaks obtained during XRD for all four conditions.

There was no evidence of the presence of any polymorphism in the synthesized PCC, except in the 200nm samples synthesized at room temperature. From Figure 20 below, the peaks marked with an asterisk it can be seen that small quantities of vaterite were found present in the sample with calcite crystals. The same sample was heated at around 80°C to see the effect of heat on the crystalline structure and the XRD repeated. Table 3 shows that heat did not change the crystalline structure significantly or reduce the relative intensity of vaterite found.
Figure 20: Evidence of Polymorphism in 200nm sample synthesized at room temperature.

Table 3: Effect of heating on Vaterite intensity in sample with polymorphism

<table>
<thead>
<tr>
<th>2 Theta</th>
<th>Relative Intensity (Before heating)</th>
<th>Relative Intensity (After Heating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.78</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>26.95</td>
<td>24</td>
<td>22</td>
</tr>
<tr>
<td>32.69</td>
<td>19</td>
<td>21</td>
</tr>
</tbody>
</table>

4.3 Emulsion Stability Study

From Figure 21 it can be seen that the emulsion droplet size did not vary considerably during the course of time. The emulsion droplet size remained on average 3.5 microns throughout the test for the system with constant agitation. For the remaining two tests without agitation, the emulsion droplet remained within the same 3.5 micron range. For
emulsion A, the emulsion droplet began to increase to 5 microns after 50 minutes. Emulsion B droplet size began to increase to 5 microns after 40 minutes.

![Graph showing emulsion droplet size over time](image)

**Figure 21:** Emulsion Stability Study; Emulsion droplet with respect to time.

Figure 22 shows an example of an image of the emulsion taken using the optical microscope after 1 minute into the experiment. Figure 23 is an example of the emulsion at final conditions after 30 minutes.
Figure 22: Light Microscope Image of mixed emulsion after 1 minute

Figure 23: Light Microscope Image of mixed emulsion after 30 minutes
4.4 Partial Volume Test

Figure 24: Partial Volume Study, Particle Diameter vs. total volume of Emulsion B added.

Figure 24 shows that the particle size remained smaller than those predicted if an equal volume of emulsion was added. This suggests that the ions tend to diffuse through to all the Emulsion A droplets evenly throughout the system. Even though the number of Emulsion A droplets are much less in quantity than the Emulsion B droplets, the calcium ions diffuse evenly throughout the system forming smaller particles with a higher yield, as opposed to larger particles with a lower yield.
CHAPTER 5

FUTURE WORK AND SIGNIFICANCE

Using emulsion membranes as a method of synthesis promises to be cost effective since the organic layer may be reused, requires minimal energy and the system does not require expensive equipment. The lower operating costs have great potential for industrial applications. Most current methods require expensive equipment and high energy consumptions. These restrictions make it difficult for large scale industrial applications.

Coalescence of emulsion droplets plays an important role in predicting the particle size. Obtaining a better understanding of coalescence of the emulsion droplets and the effect on particle size would further improve the mathematical model, thus enabling better control on particle size.

A detailed study of effects of temperature on diffusion rates, and emulsion stability would also be beneficial in predicting particle morphology and size distributions. A method to calculate transfer or reaction rates at various temperatures and concentrations will help obtaining a more accurate model to predict particle size.
CHAPTER 6
CONCLUSIONS

The double water in oil emulsion method used to synthesize precipitated calcium carbonate on a nano-scale was studied. The particles synthesized had a small particle distribution and were more regular than ground particles. The mass restriction method for controlling particle size was demonstrated although some experimental results did not fit the model very well. The main reason for the difference between model and experimental results are due to coalescence of emulsion droplets. This causes the nucleation sites within the droplets to agglomerate after the droplets have collided, therefore forming larger particles than expected. Obtaining a better understanding of coalescence of the emulsion droplets and the effect on particle size would further improve control of synthesis. The PCC synthesized via emulsion membranes formed predominantly calcite crystals, though the effect of heating should be investigated further. The method also has easily adjustable variables, such as concentration and temperature to control particle size and morphology.
APPENDIX A: SEM IMAGES

| Predicted size: 600 nm  
  Actual Size: 1115nm (mean)  
  Conditions: 60 °C |
|------------------------|
| Predicted size: 450 nm  
  Actual Size: 920nm (mean)  
  Conditions: 60 °C |
| Predicted size: 200 nm  
  Actual Size: 250nm (mean)  
  Conditions: 60 °C |
| Image | Predicted size: 600 nm  
Actual Size: 830nm (mean)  
Conditions: room temperature |
|-------|-----------------------------------------------|
| Image | Predicted size: 450 nm  
Actual Size: 467.5nm (mean)  
Conditions: room temperature |
|       | Predicted size: 200 nm  
Actual Size: 270nm (mean)  
Conditions: room temperature |
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