

**MULTI-STAGES SYNTHESIS OF  
CALCIUM HYDROXIDE PARTICLES  
FROM MALAYSIAN LIMESTONE  
BY SOL-GEL METHOD**

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FROM MALAYSIAN LIMESTONE  
BY SOL-GEL METHOD**

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Bachelor of Engineering with Honours  
(Materials Engineering)**

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## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘Multi-Stages Synthesis of Calcium Hydroxide Particles from Malaysia Limestone via Sol-Gel Method’. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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## LIST OF SYMBOLS

M	Concentration in mol/dm <sup>3</sup>
$m_{\text{CaCl}_2}$	Molarity of calcium chloride
$m_{\text{CaCO}_3}$	Molarity of calcium carbonate
$m_{\text{HCl}}$	Molarity of hydrochloric acid
$m_{\text{Na}(\text{C}_2\text{H}_5\text{O})}$	Molarity of sodium ethoxide
$\theta$	Angle in degree
$\lambda$	Wavelength in angstrom
°	Degree
%	Percentage

## LIST OF ABBREVIATIONS

C	Carbon atom
C <sub>2</sub> H <sub>5</sub> OH	Ethanol
Ca	Calcium atom
CaCl <sub>2</sub>	Calcium chloride
CaCO <sub>3</sub>	Calcium carbonate
Ca(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub>	Calcium ethoxide
Ca(HCO <sub>3</sub> ) <sub>2</sub>	Calcium bicarbonate
Ca(OH) <sub>2</sub>	Calcium hydroxide
Cl	Chlorine atom
CO <sub>2</sub>	Carbon dioxide
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
H	Hydrogen atom
HCl	Hydrochloric acid
H <sub>2</sub> O	Water
NaCl	Sodium chloride
Na(C <sub>2</sub> H <sub>5</sub> O)	Sodium ethoxide
NaOH	Sodium hydroxide
O	Oxygen atom
PSA	Particle Size Analysis
ppb	Part per billions
ppm	Part per millions
TGA	Thermogravimetric Analysis
USM	Universiti Sains Malaysia
XRD	X-Ray Diffraction

## ABSTRAK

Sintesis kalsium hidroksida,  $\text{Ca(OH)}_2$  daripada batu kapur Malaysia melalui kaedah sol-gel telah dijalankan dalam kajian ini. Ketelunan batu kapur Malaysia yang tinggi menjadikannya bahan mentah yang sesuai untuk menghasilkan sebatian kimia lain yang berasaskan kalsium. Walau bagaimanapun, pembuatan zarah  $\text{Ca(OH)}_2$  yang ketulenan tinggi bagi kegunaan perubatan masih belum wujud di Malaysia. Kaedah sol-gel telah dipilih sebagai teknik fabrikasi dalam penyelidikan ini kerana kaedah sol-gel mempunyai fleksibiliti dan prosedurnya adalah mudah dan menjimatkan kos. Bahagian pertama eksperimen melibatkan pembubaran  $\text{CaCO}_3$  dengan asid hidroklorik, HCl dan rawatan haba produk untuk mendapatkan hablur garam  $\text{CaCl}_2$  kontang. Bahagian kedua telah melibatkan tindak balas pembentukan garam antara  $\text{CaCl}_2$  dan natrium etoksida,  $\text{Na(C}_2\text{H}_5\text{O)}$  dalam medium etanol. Langkah terakhir eksperimen merangkumi hidrolisis larutan  $\text{Ca(C}_2\text{H}_5\text{O)}_2$  yang terbentuk dahulu dengan air suling untuk menjadikan zarah  $\text{Ca(OH)}_2$  dan etanol. Suspensi telah diempar untuk mengeluarkan zarah  $\text{Ca(OH)}_2$  daripada larutan. Sampel kering  $\text{Ca(OH)}_2$  dicirikan menggunakan Belauan Sinar-X (XRD), Mikroskop Elektron Pengimbasan Pancaran Medan yang dilengkapi dengan X-Ray Penyerakan Tenaga (FESEM-EDX) dan Penganalisis Saiz Zarah (PSA). Keputusan menunjukkan bahawa zarah  $\text{Ca(OH)}_2$  yang disintesis mempunyai taburan saiz yang normal dengan puncak pada 667.7 nm. Mereka mempunyai morfologi campuran batang dan bunga jagung dengan struktur nano seperti rambut pada permukaan apabila diperhatikan di bawah FESEM. Keputusan XRD menunjukkan bahawa kebanyakan  $\text{Ca(OH)}_2$  telah menjadi  $\text{CaCO}_3$  selepas terdedah kepada karbon dioksida. Secara ringkasnya, batu kapur Malaysia sesuai untuk sintesis zarah  $\text{Ca(OH)}_2$  melalui kaedah sol-gel. Parameter yang dipakai untuk pemprosesan akan mempengaruhi sifat-sifat produk yang diperolehi.

## ABSTRACT

The synthesis of calcium hydroxide,  $\text{Ca(OH)}_2$  from Malaysian limestone via sol-gel method was carried out in this study. Malaysian limestone is high purity raw material that is suitable for production of other calcium based chemical compounds. However, the manufacturing of high purity  $\text{Ca(OH)}_2$  particles for medical usages was not yet present in Malaysia. Sol-gel method was chosen as the fabrication technique used in this research because sol-gel method has great flexibilities and the procedures are generally simple and cost-saving. The first part of the experiment involved dissolution of  $\text{CaCO}_3$  with hydrochloric acid, HCl and heat treatment of the product to obtain anhydrous  $\text{CaCl}_2$  salt crystals. Second part of the experiment involved salt forming reaction between  $\text{CaCl}_2$  and sodium ethoxide,  $\text{Na(C}_2\text{H}_5\text{O)}$  in ethanol medium. The last step of the experiment is hydrolysis of the  $\text{Ca(C}_2\text{H}_5\text{O)}_2$  solution formed with distilled water into  $\text{Ca(OH)}_2$  particles and ethanol. The suspension was centrifuged to extract the  $\text{Ca(OH)}_2$  particles from the solution. The dried sample of  $\text{Ca(OH)}_2$  was characterized using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope equipped with Energy Dispersive X-Ray (FESEM-EDX) and Particle Size Analyser (PSA). Results showed that the synthesized  $\text{Ca(OH)}_2$  particles have normally distributed particle size with peak at 667.7 nm. They have rod and cornflower mixed morphology with tiny hair-like nanostructures on particle surface as observed under FESEM. XRD result indicated that most  $\text{Ca(OH)}_2$  had revert into  $\text{CaCO}_3$  after exposure to carbon dioxide. In short, Malaysian limestone is suitable for synthesis of  $\text{Ca(OH)}_2$  particles by sol-gel method. Processing parameters showed influence on properties of the product obtained.



# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

Artworks since ancient eras have great cultural significance and many efforts were performed to sustain their existences. These artworks include wall paintings, buildings such as pyramids, as well as stone sculptures. Besides facing physical erosion by nature, these artworks are now bracing themselves towards chemical corruptions by acid rains containing sulphuric, nitric as well as carbonic acid (Chelazzi, et al., 2013). Wall paintings are the most vulnerable type of artworks as they tend to delaminate from wall surface when experiencing mechanical stresses. These mechanical stresses usually arise from volumetric expansion during the formation of new salt crystals in porous network of wall (Giorgi, et al., 2010). The crystallization of salt solution produced during acidic chemical degradation of calcium carbonates beneath the surface layer will eventually cause the detachment of paint layer or more severe effects such as cracks and fissures of wall (Giorgi, et al., 2010).

Many consolidating materials were investigated and found that inorganic materials have better chemical stability than organic materials, hence providing a more securing and long-lasting consolidation effects (Giorgi, et al., 2010). In addition, dispersions of alkaline-earth metal hydroxide nanoparticles showed better performance than polymeric materials such as acrylate/methacrylate and acrylate/vinylacetate co-polymers for consolidation and protection of immovable artworks such as wall paintings and stone artifacts (Giorgi, et al., 2010; Chelazzi, et al., 2013). Most of the time, calcium hydroxide was used as primary conservative material due to their highest physiochemical compatibility with the artworks (Giorgi, et al., 2010; Chelazzi, et al., 2013). After carbonation process, these applied calcium

hydroxides will be consumed to fill up the porous network, cracks or fissures with calcium carbonates.

Dentistry is a medical field that is responsible for study, diagnosis, treatment of oral cavity. Particularly, endodontics is dental specialty that cares about dental pulp or so-called teeth. The ultimate goal for any endodontic treatment is to prevent and curb infections in pulpal and periradicular regions (Kim & Kim, 2014; Louwakukul, et al., 2017). An incomplete disinfection of the complex root canal system may result in treatment failures and persistent apical periodontitis (Nair, 2006). Many dentists are facing difficulties in achieving a full disinfection solely with mechanical instruments. As a result, disinfection via chemical route was introduced.

The first pulp-capping agent introduced was calcium hydroxide due to its excellent antimicrobial properties, tissue-dissolving ability and hard tissue formation ability. Calcium hydroxide is termed as a good antimicrobial agent because it can dissociate in aqueous solution to provide high pH environment (Louwakukul, et al., 2017). The bacterial growth will be retarded when the environment become highly basic, and the occurrence of local bacterial infections can be minimized. Besides, calcium hydroxide can provide protection for a longer duration owing to its low solubility limit in tissue fluids when in direct contact with vital tissues (Kim & Kim, 2014). Therefore, calcium hydroxide was widely applied in dental application as a medicament for pulp capping, apexogenesis, apexification, root canal sealer and inter-appointment dressings until present-day (Kim & Kim, 2014).

Nanomaterials are materials with at least one external dimension falls in nanoscale or having internal or surface structure in nanoscale. According to the definition from ISO/TS 80004, nanoscale is defined as dimension between 1 nm to 100 nm. Nanomaterials exist in various forms, including nanoparticles, nanofibers,

nanorods, nanotubes, nanoplates, nanocomposites and nanoporous material. Nanomaterials with extremely small sizes can easily cross biological membranes and gain access to bloodstream, cells, tissues and organs that cannot be achieved by larger sized particles (Allaker & Ren, 2008). This implies that the smaller the particle size of calcium hydroxide, the better their penetration power into smaller and complex networks of wall cracks and pulp cavities. Better penetration of calcium hydroxide into artwork cracks ensures a better recovery of cracks with less internal flaws whereas better penetration of calcium hydroxide into complex pulp cavity of dentine ensures a better disinfection and lower chance of inflammation.

Calcium hydroxide nanoparticles can be obtained from two fundamental processes which are bottom-up and top-down methods (Chelazzi, et al., 2013). Top-down approach involves the breaking down of starting materials with larger sizes via grinding or thermal decomposition into desired smaller particles. Top-down synthesis method generally has high production yield but with limited particle size range. On the other hand, bottom-up process involves the precipitation and growth of solid crystals from the liquid phase containing the precursors when saturation point is exceeded. This initiative shows advantages in tailoring the morphologies, properties and particle size of the synthesized product (Zhu, et al., 2019). Besides, the synthesis route is more flexible because different precursors can be used to produce the same final product.

## **1.2 Problem Statement**

Several synthesis routes of calcium hydroxide nanoparticles were proposed and investigated in the past. One of the methods to produce calcium hydroxide is by reacting the water directly with calcium oxide. However, direct reaction between

calcium oxide with water under normal condition will form a passivated surface layer of hydroxides, preventing the complete conversion of calcium oxides into calcium hydroxides (Chelazzi, et al., 2013).

Preparation of tiny calcium hydroxide particles can also be performed by grinding and dispersion of slaked lime in water. The particle size obtained with this approach ranges from 300 nm to 800 nm, which limited the penetrating ability of the synthesized particles (Giorgi, et al., 2010; Chelazzi, et al., 2013). Thermo-mechanical method was also used to produce calcium hydroxide. The slaked lime is mechanically grinded in hot rolling mill, producing large amount of particles that does not require further purification (Chelazzi, et al., 2013). However, this method has a limitation where the particle size distribution is limited. The particles obtained with such method are hexagonal platelets with average dimension of around 150 nm to 300 nm.

Besides top-down synthesis routes mentioned before, bottom-up synthesis of calcium hydroxide was also studied by many researchers. One of these includes reaction between calcium chloride and sodium hydroxide solution in water at temperature of 90 °C which produces hexagonal nanoplates with sides of 100 nm to 250 nm and thickness of 2 nm to 40 nm (Ambrosi, et al., 2001). However, the result showed that the particles have high degree of agglomeration. This is because calcium hydroxide has tendency to aggregate in water. A deduction was made where smaller particle size ensures a greater stability of their dispersions (Ambrosi, et al., 2001).

Salvadori & Dei (2001) once proposed that higher reacting temperature yields more calcium hydroxides. They performed a synthesis pathway using ethylene and propylene glycol as solvent and successfully yield a higher calcium hydroxide amount when filtrated at higher temperature. The extracted calcium hydroxides are nano-sized (30 nm to 60 nm) platelike crystals. However, the purification of glycols is lengthy

due to adsorption onto particle surfaces (Giorgi, et al., 2010). In contrast, short chain alcohols provide kinetically stable dispersions when used as dispersants during synthesis of calcium hydroxide (Giorgi, et al., 2010).

Another research using calcium nitrate and sodium hydroxide to synthesize calcium hydroxide nanoparticles in ethylene glycol was performed. The particles obtained has hexagonal morphology and are reasonably stable over time under standard temperature and pressure (Roy & Bhattacharya, 2010). The experiment is later repeated with modifications where the medium was changed to water (Harish, et al., 2021). Findings once again verified that calcium hydroxide forms agglomeration in water although nanoparticles were formed.

Another alternative in producing calcium hydroxide includes reacting the metallic calcium with short chain alcohols such as ethanol and propanol to form alkoxides (Poggi, et al., 2016). Calcium alkoxides are first formed at high temperature and pressure, followed by hydrolysis of the formed compound into calcium hydroxide nanoparticles, given that using calcium alkoxide for calcium hydroxide nanoparticle synthesis showed a promising result since previous research (Favaro, et al., 2008).

Malaysia has plenty of limestone resources that could be used as starting materials for synthesis of calcium hydroxide particles. However, the manufacturing of high purity calcium hydroxide particles for medical usages was not yet present in Malaysia. If the sol-gel synthesis method was selected, the manufacturing process should be cost-friendly and will generate the least amount of waste so that it is commercially feasible.

### 1.3 Research Objectives

The main objectives of this study are:

- i. To synthesize calcium hydroxide,  $\text{Ca(OH)}_2$  particles using the Malaysian limestone as calcium precursor by sol-gel method.
- ii. To investigate multi-stages synthesis route that yields various products with commercial values.
- iii. To study the influence of molar ratio, solvent volume and additives on properties of products formed.

### 1.4 Thesis Outline

**Chapter 1** introduces the research background of this paper. The problem statement and objectives for current studies are also stated in this chapter as well.

**Chapter 2** provides a variety of literature reviews related to current study. This includes basic information, properties and applications of related chemical compounds and some information about nanomaterials as well as sol-gel synthesis method.

**Chapter 3** elaborates the methodology in synthesizing calcium hydroxide nanoparticles from Malaysian limestone via sol-gel method and the characterization techniques used to analyse the synthesized powder samples.

**Chapter 4** includes all the observation and findings of current research. Scientific discussions about the experimental outcome was carried out and the inferences made are presented in this chapter.

**Chapter 5** consists of general conclusion about this research and some recommendations for future work in current field.

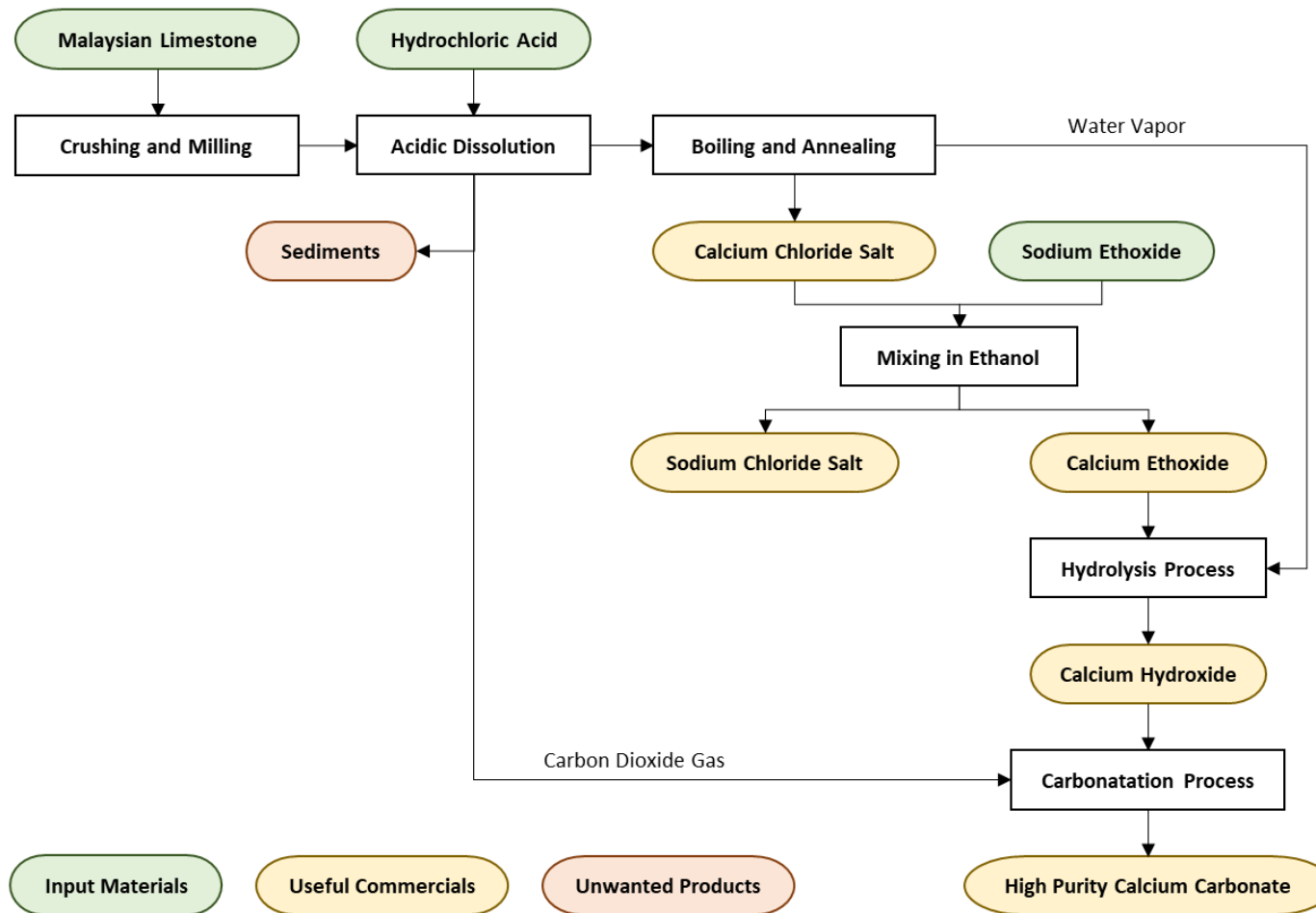


Figure 1.1 Schematic diagram showing the general concepts of the research performed

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Limestone, $\text{CaCO}_3$

Limestones are sedimentary carbonate rocks with majority minerals of calcite, the calcium carbonate,  $\text{CaCO}_3$  with trigonal crystal structure (Šiler, et al., 2018). Each compound has one calcium,  $\text{Ca}^{2+}$  ion and a carbonate,  $\text{CO}_3^{2-}$  ion. About 20% to 25% of sedimentary rocks are carbonate rocks and most of them are limestone. The remaining carbonate rocks are dolomite which was also called magnesian limestone. Dolomite mineral contains significant percentage of magnesium, Mg and have a chemical formula of  $\text{CaMg}(\text{CO}_3)_2$ . They were formed when magnesium replaces the calcite or lime mud before lithification process.

Most limestone originated from seas and rock-forming organisms. They are also found in fresh waters, lakes, rivers and caves containing dissolved calcium (Šiler, et al., 2018; Hobart, Accessed on 12 June 2022). They form naturally when calcium ion is precipitated out from the water. On the other hand, limestone can also be formed through evaporation process. The product from such process includes stalactites and stalagmites which were cumulatively called “speleothems”. When the water droplets containing dissolved calcium bicarbonate,  $\text{Ca}(\text{HCO}_3)_2$  were evaporated, water molecules were removed while leaving the calcium carbonate behind. They will be deposited and accumulated to form icicle-shaped structures over time. The morphologies of stalagmite formed are mostly determined by the drip rate of precipitating carbonates (Frisia, 2019). Figure 2.1 shows the image of cave roof in Ruakuri Cave with high density of conical stalactites.





Figure 2.1 Cave roof with high density of conical stalactites in Ruakuri Cave, Waitomo, New Zealand (Frisia, 2019)

### 2.1.1 Malaysian Limestone

Malaysian limestone appeared naturally with different features and shapes due to differential chemical erosion by rainwaters. The states of Kelantan, Perak, Pahang, Kedah and Perlis have high percentage of limestone hills but there are only a few hills present in Terengganu, Selangor and Negeri Sembilan. Most territories including Selangor, Johor and Kuala Lumpur have significant quantities of limestone bed rock where the limestone was buried underground (Bakhshipouri, et al., 2008). Figure 2.2 shows the distribution of limestone in Malaysia Peninsular where the red colour regions are limestone-rich area.

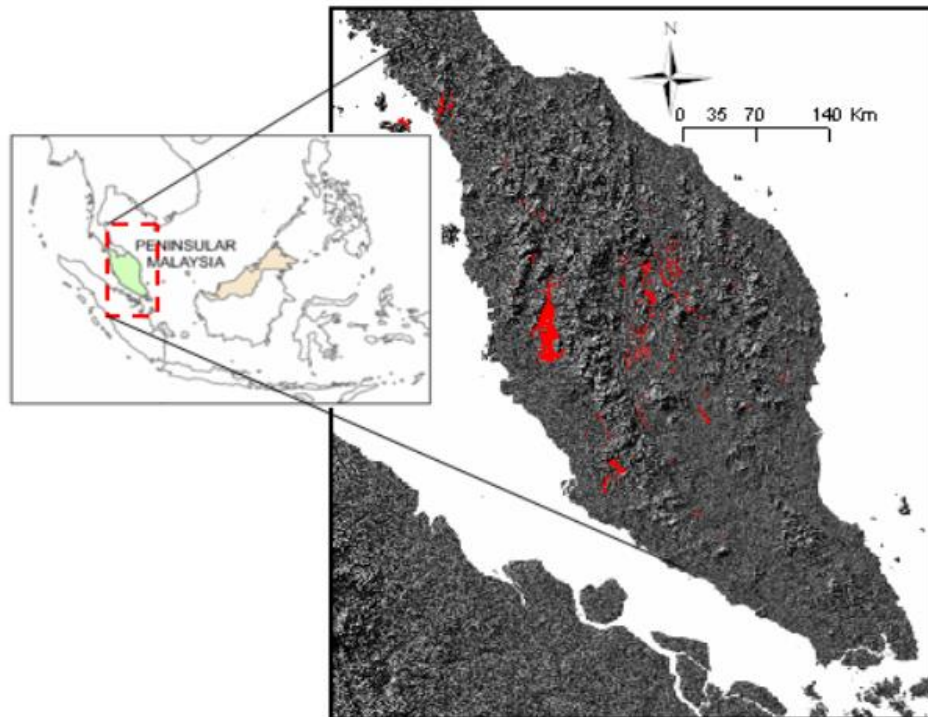


Figure 2.2 Distribution of limestone (red colour) in Malaysian Peninsular (Bakhshipouri, et al., 2008)

Karst is a topography formed from the dissolution of soluble rocks by rainwater or underground drainage. The landscape may result in a variety of features both on the surface and beneath the ground. The feature produced includes limestone pavement, sinkholes, disappearing streams, reappearing springs, remnant hills, pinnacles and caves

(Bakhshipouri, et al., 2008). Batu Caves in Malaysia which was one of tourism attractions is the result from the weathering and chemical dissolution of limestone hills. Figure 2.3 shows typical morphological features for five classes of karstic ground condition whereas Figure 2.4 shows the limestone plateau dissected deeply by dissolution of carbonates.

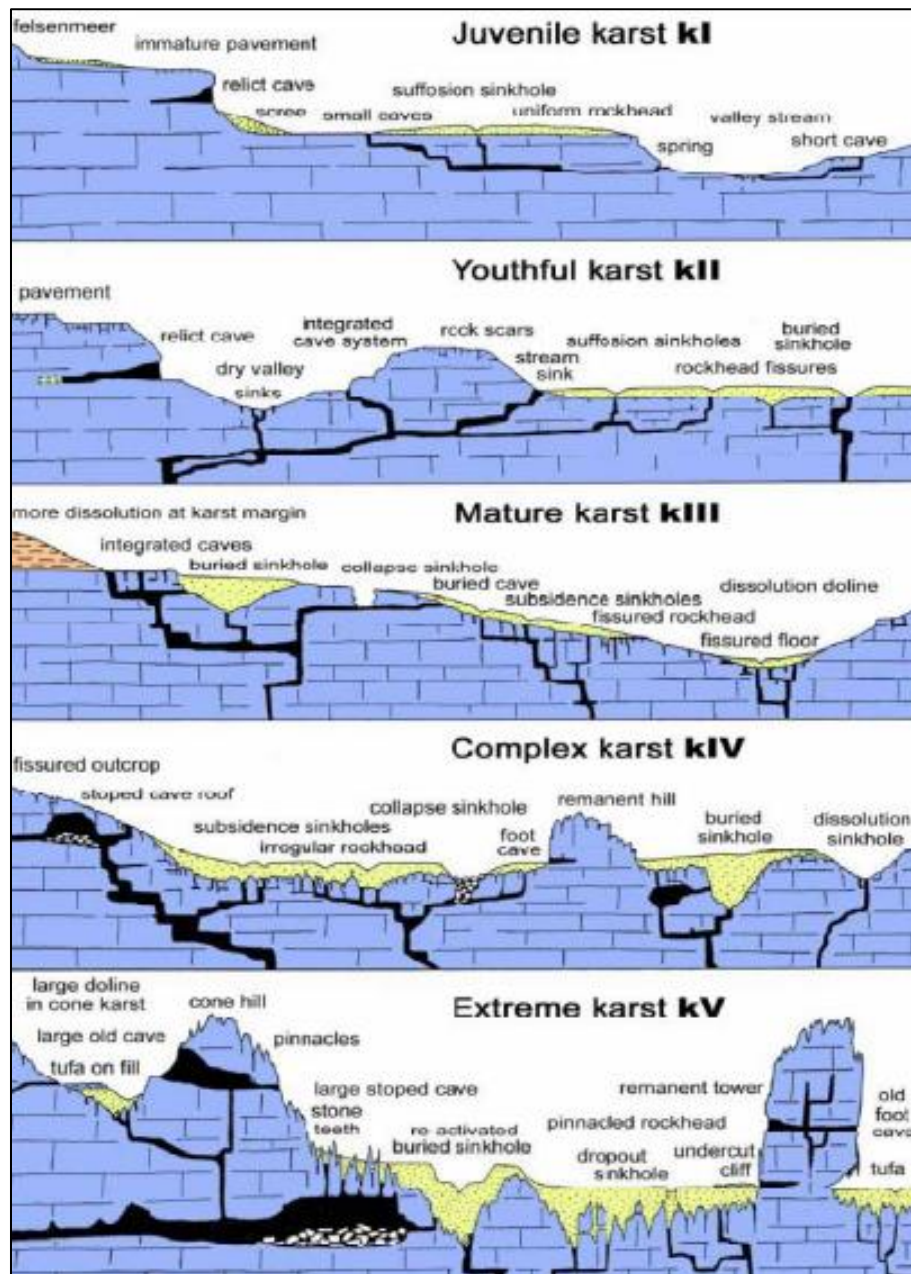


Figure 2.3 Typical morphological features for five classes of karstic ground condition (Bakhshipouri, et al., 2008)

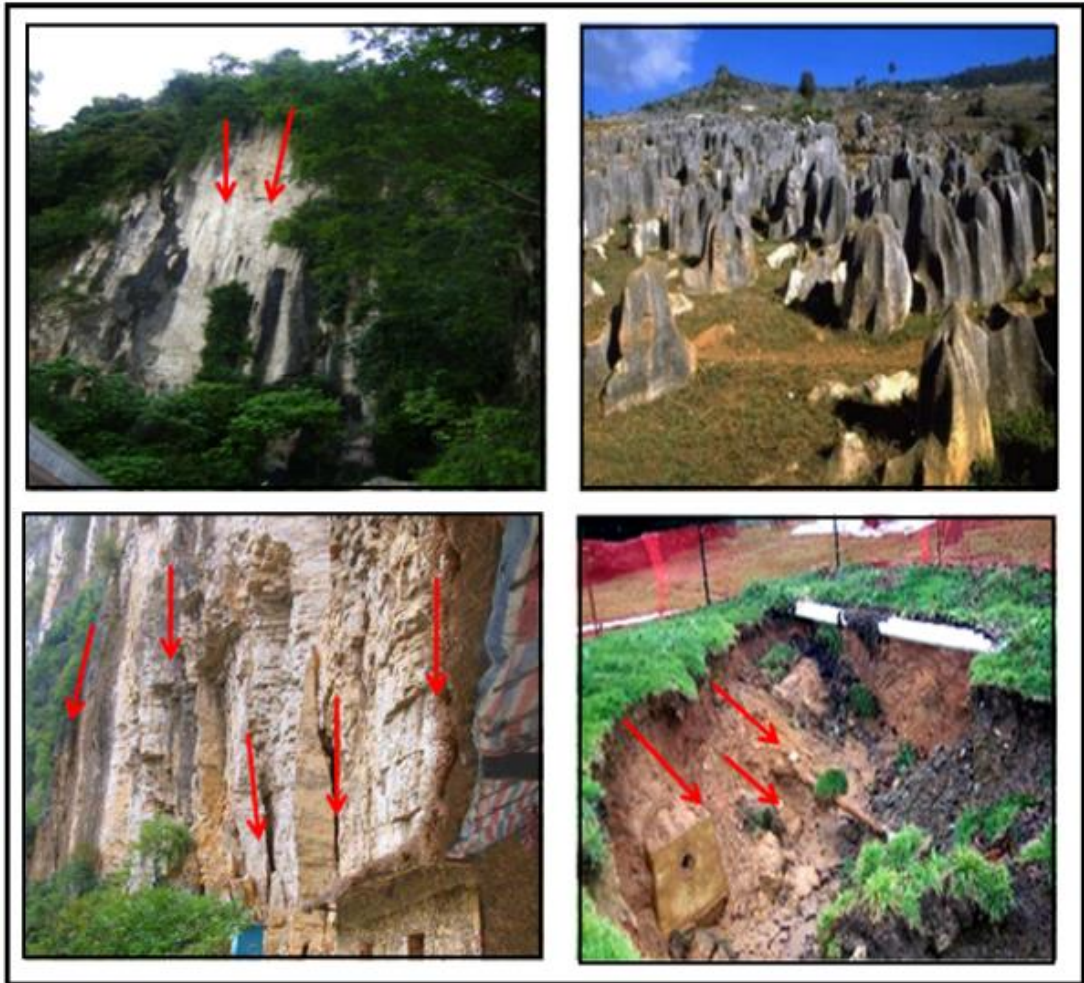


Figure 2.4 Originally flat limestone plateau dissected deeply by dissolution (Bakhshipouri, et al., 2008)



### 2.1.2 Properties of Limestone

Calcium carbonate has several polymorphic modifications with calcite and aragonite as the most abundant naturally occurring phases (Šiler, et al., 2018). Most lime contains impurities such as clay, sand, carbonates, phosphates or other iron-containing minerals and rarely occur as high purity mineral (Šiler, et al., 2018). They can be further classified into chalk, coquina, crystalline limestone (marble), dolomitic (magnesium-rich) limestone, fossiliferous limestone, lithographic limestone, oolitic limestone, travertine and tufa, depending on their morphologies and compositions (Hobart, Accessed on 12 June 2022). It is difficult to differentiate among carbonate minerals as they have similar physical properties. The identification of the rock can be aided by specific gravity and crystal form if they are relatively monomineralic and compact. The rate of solubility of different carbonates in dilute hydrochloric acid are different hence become a useful identification technique (Robert, et al., 2006).

Calcium carbonate has three general chemical reactions. Firstly, they react readily with acids to form carbonic acid which will quickly disintegrate into carbon dioxide and water molecules. This corrosion mechanism can be seen on building walls or stone artifacts exposed to rainwaters containing acids such as sulphuric acid, nitric acid and carbonic acid. Secondly, calcium carbonate will undergo thermal decomposition when heated to temperature above 840 °C and carbon dioxide gas will be released during the reaction (Giorgi, et al., 2010). A porous calcium oxide structure will be left behind after the calcination. As for the third reaction, calcium carbonate absorbs dissolved carbon dioxide in water to form soluble calcium bicarbonate. This mechanism is responsible for the erosion happening in carbonate rocks and formation of speleothems. Figure 2.5 shows the aforementioned chemical reactions of calcium carbonate with their respective balanced equations.

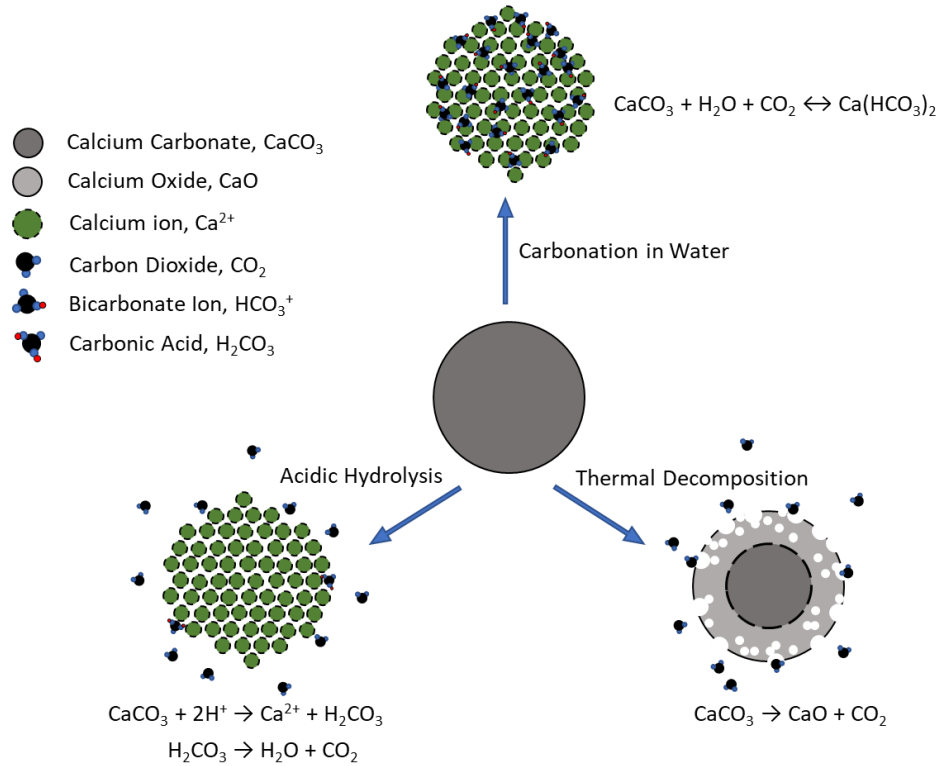


Figure 2.5 Schematic diagram of reactions associated with calcium carbonate

### 2.1.3 Applications of Limestone

Calcium carbonate has a wide variety of usages, including building materials in construction, fluxing agent in ores purification, fillers and extenders as well as acidity regulator in agriculture.

#### 2.1.3(a) Construction

The application of limes in construction can be dated back to 4000 BC when Egyptians used it for plastering the pyramids (Oates, 1998; Giorgi, et al., 2010). Over the centuries, limestone played an important role as an aggregate in lime-based and cement-based concrete. The demand for limestone increased rapidly since development of Portland cement in the 19<sup>th</sup> century. Since then, limestone not only been used as aggregates in construction site, besides also used as primary raw material in production of Portland cement (Oates, 1998).

### **2.1.3(b) Ores Purification**

Calcium carbonate can be used to separate impurities from raw mineral ores during metal refining process. They will decompose into calcium oxide that forms basic molten slag on molten metal surface. Impurities from the ore will then be dissolved and eliminated together with the slag, leaving high purity molten metals behind (Oates, 2005).

### **2.1.3(c) Fillers and Extenders**

Very finely divided and precipitated high purity limestones are usually used as fillers or extenders in other materials to improve their performance (Oates, 1998). They were added onto paper to increase paper brightness and opacity. As for paint, limestones were mixed in to reduce shrinkage on hardening and improve adhesion onto surface. Besides, calcium carbonate can act as flame retarder in rubber as they decompose and release carbon dioxide gas when heated.

### **2.1.3(d) Agriculture**

In most of the time, limestone is applied directly to the soil in agriculture. Their ability to dissolve and hence maintaining the pH level of soil near neutrality for a prolonged duration makes them a good candidate as pH regulator in farmland. As mentioned before, calcium carbonate reacts readily with acids to form corresponding salts and water while liberating carbon dioxide gas. Besides, limestone helps replenishing the calcium and magnesium consumed by the crops (Oates, 2005).

## 2.2 Calcium Hydroxide

Calcium hydroxide,  $\text{Ca}(\text{OH})_2$  which was commonly known as slaked lime or limewater is an inorganic compound that contains a calcium,  $\text{Ca}^{2+}$  ion and two hydroxyl,  $\text{OH}^-$  ions. They are colourless crystals or white powders formed when calcium oxide is hydrolysed with water. The formed hydroxides are either dry powder or lime putty depending on water amount added (Giorgi, et al., 2010). The naturally occurring calcium hydroxide is portlandite with hexagonal crystal structure.

### 2.2.1 Properties of Calcium Hydroxide

Calcium hydroxide,  $\text{Ca}(\text{OH})_2$  can dissociate in aqueous solution to release calcium,  $\text{Ca}^{2+}$  ion and hydroxyl,  $\text{OH}^-$  ions which will subsequently provide a strong basic solution with high pH value. However, its solubility decreases as the pH level of the solution increases. This is due to common ion effect of hydroxyl,  $\text{OH}^-$  ions present in the solution. The deposition of calcium hydroxide from solution can best described with setting of Portland cement. Calcium hydroxides are first formed by hydrolysis of calcium oxide with plenty of water to form putty. As the water amount decreases due to evaporation, the pH level of the mixture increases with its concentration. The precipitation of calcium hydroxide onsets when the saturation point is exceeded.

Besides, calcium hydroxide will undergo carbonation process when exposed to atmospheric or water-dissolved carbon dioxide. Carbon dioxide gas is consumed by calcium hydroxide to revert into calcium carbonate (Giorgi, et al., 2010). This is a potential mechanism to reduce and recover carbon content in atmospheric air. On the other hand, calcium hydroxide can be reverted into calcium oxide by thermal decomposition at elevated temperature. Figure 2.2 below shows the schematic diagram of reactions associated with calcium hydroxide.



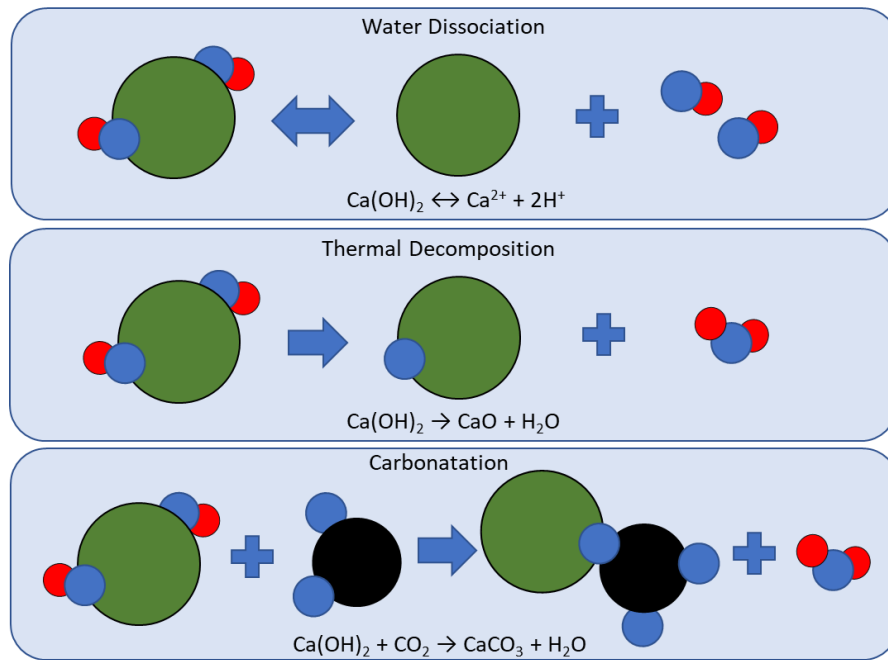


Figure 2.6 Schematic diagram of reactions associated with calcium hydroxide

## 2.2.2 Applications of Calcium Hydroxide

Calcium hydroxide with excellent properties had gained attention from various fields. This includes their application in artworks conservation, dentistry, food processing industry and agriculture (Harish, et al., 2021).

### 2.2.2(a) Artworks Conservation

Artworks since ancient eras have great cultural significance and many efforts were performed to sustain their existences. Besides facing physical erosion, carbonate-based artworks are bracing themselves towards chemical corrosions by acid rains containing sulphuric, nitric as well as carbonic acid (Chelazzi, et al., 2013). The corrosion had caused a loss in carbonate or delamination of paint layers as shown in Figure 2.7 where the detachment of paint layer is mainly caused by mechanical stress manifested by salt crystallization.



Figure 2.7 Salt efflorescence on surfaces of mural paintings and detachment of the paint layer (Chelazzi, et al., 2013)

A typical wall painting consists of roughly three layers as shown in Figure 2.8 where the main components are calcium carbonate formed by reaction of the lime with atmospheric carbon dioxide gas. Sand was added to lime as filler in Arriccio layer to prevent shrinkage and cracking upon drying besides providing mechanical strength to the plaster (Chelazzi, et al., 2013). The intermediate layer called Intonaco layer usually has equal amount of lime and sand whereas the outer layer was the paint layer. The paint layer is a thin film made by mixture of colour pigments and lime which upon carbonatation process will embedded into the crystalline carbonate network.

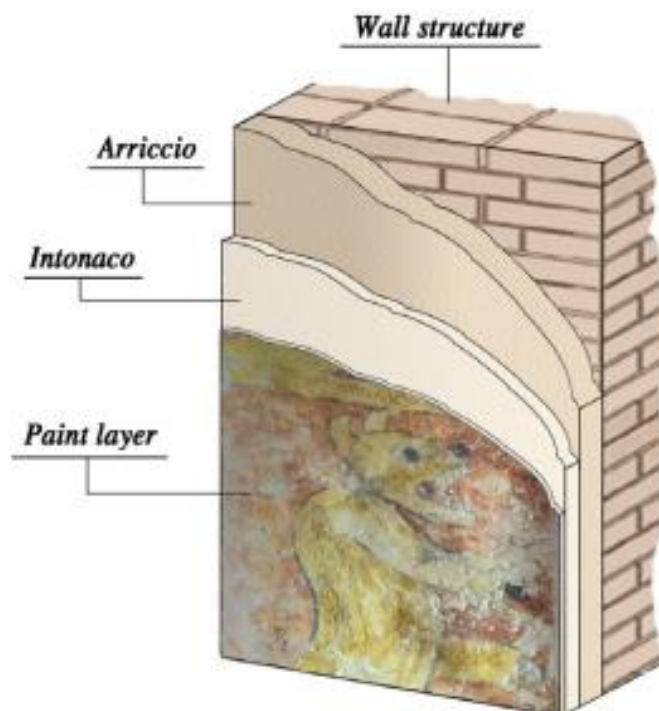


Figure 2.8 Stratified model of wall painting with multi-layers (Chelazzi, et al., 2013)

Therefore, calcium hydroxide was used as primary conservative material due to their highest physiochemical compatibility with the artworks (Giorgi, et al., 2010; Chelazzi, et al., 2013). After carbonatation process, these applied calcium hydroxides will be consumed to fill up the cracks or fissures with calcium carbonates.

Besides, nanoparticles of calcium or magnesium hydroxide are used to perform deacidification treatments for cellulose-based works of art (Poggi, et al., 2016). This is because cellulose degradation mechanisms induced by metal ions and acidity can be effectively stopped by neutralization with calcium hydroxide. This method has an advantage where the catalytic activities of metal ions will become much slower near neutrality (Strlič, et al., 2003).

### 2.2.2(b) Dentistry

Dentistry is a medical field that is responsible for study, diagnosis, treatment of oral cavity. Particularly, endodontics is dental specialty that cares about dental pulp or so-called teeth. Figure 2.9 shows the schematic diagram of procedures in dental treatment of infected pulp. An opening was first made on the enamel, followed by removal of infected tissues inside the pulp cavity. The canal was then cleaned and disinfected using dental medicaments before refilling the cavity with gutta percha, a thermoplastic latex derived from a tree. Finally, the opening was sealed with artificial crown, which was a thin, plastic coating painted on the chewing surfaces of teeth.



Figure 2.9 Schematic diagram of procedures in dental treatment of infected pulp

Calcium hydroxide was widely applied in dental application as an intracanal medicament for pulp capping, apexogenesis, apexification, root canal sealer and inter-appointment dressings (Law & Messer, 2004; Cwikla, et al., 2005; Ercan, et al., 2006; Kim & Kim, 2014). It shows a good antimicrobial properties as the bacterial growth will be retarded when the environment become highly basic, and the occurrence of local bacterial infections will be minimized. A research had proved that very high pH level is required to retard and prevent any bacterial growth during dental operations (McHugh, et al., 2004). Moreover, calcium hydroxide particles with nano size have better antimicrobial effect than conventional ones and smaller amount is required when in use (Dianat, et al., 2015).

#### **2.2.2(c) Food Processing Industry**

Calcium hydroxide has been deployed in food processing industry because it has lower toxicity and mild basic properties compared to other earth-metal hydroxides. One function of calcium hydroxide in food industry is to moderate the pH level of the processed commercials. For example, they were used in production of alcoholic beverages and soft drinks.

#### **2.2.2(d) Agriculture**

Similarly with calcium carbonate, calcium hydroxide also played an important role in maintaining the pH level of soil. The main difference between calcium hydroxide and calcium carbonate is their behaviour when in action. Calcium carbonate can only reduce acidity of soil to near neutrality. In contrast, calcium hydroxide can convert acidic farmland into mild or highly basic farmland.

## **2.3 Calcium Chloride**

Calcium chloride,  $\text{CaCl}_2$  is an ionic halide compound that exists as white crystalline solid or powder at ambient room temperature. Each  $\text{CaCl}_2$  compound consisted of one calcium,  $\text{Ca}^{2+}$  ions and two chloride,  $\text{Cl}^-$  ions. Anhydrous  $\text{CaCl}_2$  are rarely found as naturally occurring minerals in nature but their derivate hydrate complexes namely sinjarite, a dihydrate and antarcticite, a hexahydrate can be found around dry lakes and brines (Ropp, 2013).

The  $\text{CaCl}_2$  salt solution can be chemically synthesized by dissolving the calcium carbonate,  $\text{CaCO}_3$  with hydrochloric acid,  $\text{HCl}$  or produced as by-product from Solvay Process, a process performed to obtain soda ash from brine. Pure anhydrous  $\text{CaCl}_2$  salt cannot be prepared directly from boiling the solution at atmospheric pressure because a eutectic point that favours the precipitation of dihydrate solid phases from the solution is present (Ropp, 2013). Further treatment such as annealing of the precipitated salt is required to obtain the high purity anhydrous  $\text{CaCl}_2$  salt crystals.

### **2.3.1 Properties of Calcium Chloride**

Calcium chloride,  $\text{CaCl}_2$  salt shows a high solubility in aqueous solution unlike most of other insoluble calcium compounds. They can dissolve readily in water or even moist to release free moving calcium,  $\text{Ca}^{2+}$  ions and chloride,  $\text{Cl}^-$  ions in the solution. Due to highly exothermic nature, the dissolving of  $\text{CaCl}_2$  salt liberates large amount of heat energy and this could raise the solution temperature to around  $60\text{ }^\circ\text{C}$  (Ropp, 2013). The exothermic nature for dissolution of  $\text{CaCl}_2$  salt crystal is due to its strong hygroscopic properties. They tend to attract and absorb water molecules from nowhere to form hydrate complexes which is relatively more stable than anhydrous form. When the  $\text{CaCl}_2$  salt was heated to molten state, it can be electrolysed to produce elemental calcium,  $\text{Ca}$  metal and chlorine,  $\text{Cl}_2$  gas (Ropp, 2013).

### **2.3.2 Applications of Calcium Chloride**

Calcium chloride,  $\text{CaCl}_2$  salt has some useful properties such as strong hygroscopic properties and highly exothermic dissolution reaction. These properties are carefully tailored and utilized for their applications in various fields. Their application includes desiccant, freeze suppressor, dust reduction and heating packages.

#### **2.3.2(a) Desiccant**

The salt of calcium chloride,  $\text{CaCl}_2$  possesses a strong hygroscopic properties, making them one of the most commonly used desiccant to remove moisture from atmosphere (Ropp, 2013). As explained in above, anhydrous form of  $\text{CaCl}_2$  salt is metastable and is vulnerable to moist. It tends to attract and react with water molecules to form hydrate complexes which is much more stable. As a result, dry atmosphere can be achieved as the moisture from atmospheric air is entrapped in  $\text{CaCl}_2$  hydrate complexes.

#### **2.3.2(b) Freeze Suppressor**

Calcium chloride,  $\text{CaCl}_2$  is one of many de-icing agents that can be used to lower down the freezing point of water, hence preventing occurrence of freezing (Ropp, 2013). In order to perform de-icing,  $\text{CaCl}_2$  salt powders are spread onto the ice surface. When these salt powders were dissolved in water or moist, plenty of heat energy will be liberated due to exothermic dissolution reaction of anhydrous  $\text{CaCl}_2$  salt. The heat energy released will progressively melt the ice until thermal equilibrium is reached. Moreover, addition of aqueous  $\text{CaCl}_2$  into the solution can effectively lower the freezing point of solution to as low as  $-52\text{ }^\circ\text{C}$  which prevent freezing of water at normal freezing point (Farnam, et al., 2015).

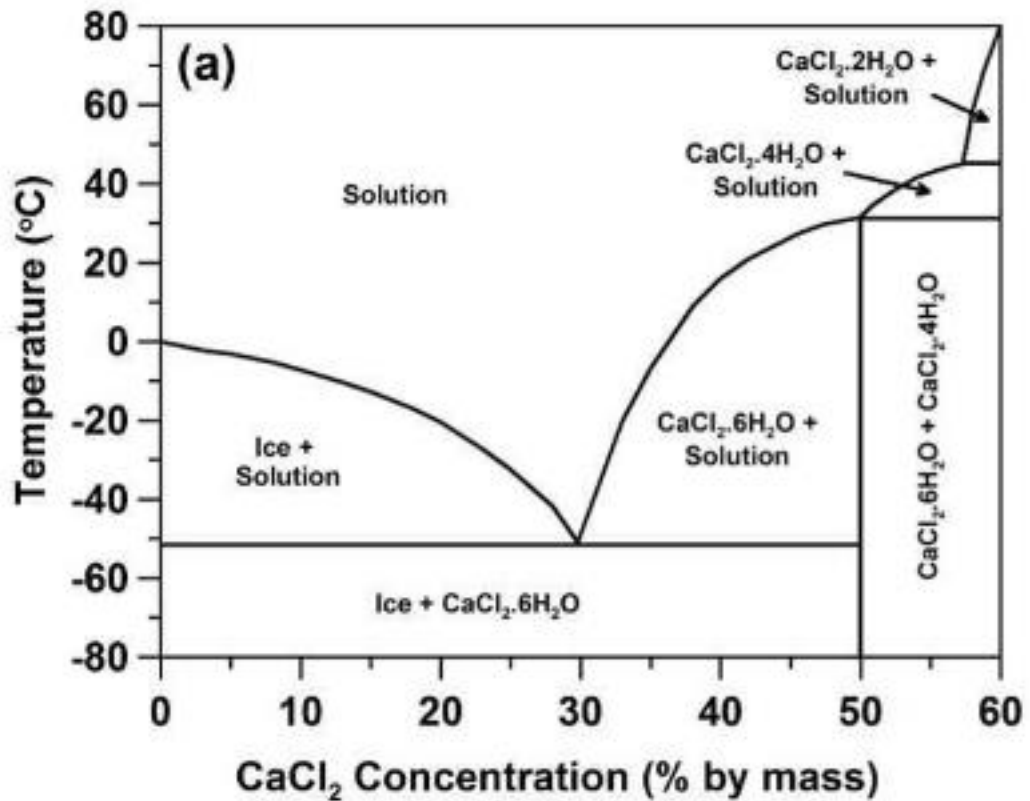


Figure 2.10 Phase diagram for  $\text{CaCl}_2 - \text{H}_2\text{O}$  binary system (Farnam, et al., 2015)

### 2.3.2(c) Dust Reduction

By utilizing the hygroscopic properties of calcium chloride,  $\text{CaCl}_2$  salt, we can also use  $\text{CaCl}_2$  salt to reduce the airborne dust particulates amount. When  $\text{CaCl}_2$  was spread evenly onto the road surface, a thin liquid layer will be formed as  $\text{CaCl}_2$  absorbs water rapidly to form hydrate complexes in normal condition. This liquid layer formed with good wettability tends to hold tight on dusts, preventing them from escaping into air as airborne particulates. As a result, atmospheric dust amount can be decreased.