SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA

CHARACTERISTIC AND POTENTIAL OF PERLIS CARBONATE ROCK IN THE DOWNSTREAM INDUSTRIES

by

MUHAMMAD ANWAR BIN ABD RAHIM

Supervisor: Assoc. Prof. Dr. Kamar Shah Bin Ariffin

Dissertation submitted in partial fulfillment
of the requirements for the degree of Bachelor of Engineering with Honours
(Mineral Resources Engineering)

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘Thesis Title’. 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.

Name of Student:	**Muhammad Anwar Bin Abd Rahim**	Signature:
Date:		

Witness by

Supervisor:	Assoc. Prof. Dr. Kamar Shah Bin Ariffin	Signature:
Date:		

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Muhammad Anwar Bin Abd Rahim

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LIST OF SYMBOLS

cm	Centimeter
cm^{-1}	Reciprocal centimeter
Mt	Million tons
°C	Degree celcius
K	Kelvin
MPa	Mega Pascal
ml	milliliter
mm	millimeter
kN	Kilo Newton
g	gram
mg	milligram
µm	micron
Δt	Temperature change

LIST OF ABBREVIATIONS

atm	Atmospheric pressure
FTIR	Fourier transform infrared
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
SEM	Scanning electron microscope
TG	Thermogravimetric
DTA	Differential thermal analysis

ABSTRAK

Sampel batu karbonat dari Chuping Perlis, Malaysia telah dianalisis untuk mengetahui kegunaan dan potensinya dalam industri hiliran seperti kaca, simen, pertanian, pembinaan, dan pembuatan keluli. Pemeriksaan kimia komposisi batuan karbonat mendedahkan bahawa lebih daripada 90 peratus komposisi batuan adalah kalsium oksida (CaO), yang menunjukkan bahawa komposisi karbonat dalam batu tersebut adalah tinggi. Sampel batu itu juga telah diuji dengan asid hidroklorik (HCL) untuk melihat kereaktifan terhadap asid diatas permukaannya. Ujian beban titik juga dilakukan untuk mengukur kekuatan batu tersebut. Untuk menentukan kesan prosedur pengkalsinan terhadap ciri-ciri batu itu, sampel batu telah dikalsinkan bagi melihat perubahan fizikal dan kimia yang berlaku keatas batu tersebut. Penyiasatan difraksi sinar-X dan spektrum inframerah transformasi Fourier mendedahkan bahawa rawatan haba terhdap sampel batu telah membuat perubahan yang ketara kepada penghapusan fasa $CaCO_3$, yang membentuk komposisi CaO. Mikrofotograf mikroskop elektron pengimbasan juga mendedahkan bahawa proses pengkalsinan batu kapur secara drastik mengubah ciri morfologi, yang mengakibatkan penghasilan permukaan yang berliang dengan zarah sfera kecil. Ujian susut dan kereaktifan juga dijalankan untuk mendedahkan gred batu kapur bagi kegunaan industri. Berdasarkan kualiti fizikalnya yang menggalakkan, keputusan projek menunjukkan bahawa batu kapur Chuping Perlis mempunyai potensi besar untuk digunakan dalam pelbagai sektor hiliran.

ABSTRACT

Carbonate rocks from Chuping, Perlis, Malaysia was analysed for their prospective application in the downstream industries such as glass, cement, agriculture, construction, and steelmaking. The composition chemical examinations of carbonate rocks reveal that greater than 90 percent of the rocks' composition is calcium oxide (CaO), indicating that the composition carbonate in rock is high. The sample are also being studied with hydrochloric acid (HCL) to detect the surface reactivity. The point load test is also performed to measure the sample's strength. To determine the influence of the calcination procedure on the characteristics of sample, the sample was calcined. The investigations of X-ray diffraction and Fourier-transform infrared spectra revealed that heat treatment of sample significantly contributed to the elimination of the $CaCO_3$ phase, resulting in the formation of the CaO form. The scanning electron microscopy microphotographs of sample revealed that the calcination process drastically altered the morphological features, resulting in the production of a highly porous surface with minute spherical particles. The decrepitating and reactivity tests revealed the industrial grade of the rock. Based on its favourable physical qualities, the results indicated that Perlis rock has significant potential for use in a variety of downstream sectors.

CHAPTER 1

INTRODUCTION

1.1 Introduction

$CaCO_3$ is the chemical formula for carbonate rock, a sedimentary carbonate rock comprised of calcium and magnesium carbonate. It may replace for limestone in several fields and businesses, including cement manufacture, the pharmaceutical industry, road building materials, glass industries, refractory steel production, and downstream industries. Dolomite is the second most prevalent carbonate mineral in Malaysia, behind limestone, and is mostly utilized as an aggregate for road building and soil fertilizer. There were four dolomite quarries in Malaysia, of which three were in Perlis. Approximately 600 million tons (Mt) worth of dolomite were reserved (NST, 2015). As dolomite shares many of the same qualities as calcite and limestone, it appears that the local dolomite has great exploration potential. Therefore, it is necessary to investigate and implement the use of dolomite in several sectors to enhance the variety.

Dolomite is a carbonate mineral composed of calcium magnesium carbonate that is anhydrous. It is an important constituent of dolostone and dolomitic marble. It is a vitreous, pearlescent mineral that is available in several hues, including white, pink, green, brown, and black, among others. It is utilized in the building sector as an alternative for limestone. Dolomite is primarily used as a refractory and later as a flux in the steel and iron industries. In its calcined form, it is utilized as a steelmaking slag flux, where, in addition to boosting slag fluidity, its magnesium content protects and prolongs the life of the refractory linings of steel vessels. Consequently, calcined dolomite held the greatest share of the market in 2019 (Grand View Research, 2022).

Glass and ceramics are other significant market end-user categories. Along with dolomite and limestone, lime is added to the glass melt. The mineral's magnesia content strengthens the glass and prevents devitrification, which is important in the production of flat glass. It is also used in the manufacture of container glass.

The Department of Minerals and Geoscience Malaysia Kedah/Perlis/Penang discovered dolomite rock of the finest grade in the northern portion of the state, therefore enabling Perlis to have high-value mineral assets, such as gold, if they are marketed. Its director, Zainol Husin, stated that the finding revealed that if dolomite was processed, it might yield a chemical called "Magnesium Oxide" (MgO) that is sold at a premium on the market (NST, 2015).

This study aims to explore the properties and possibilities of Perlis carbonate rock for industrial applications. A tiny amount of carbonate rock sample was used in an experiment to investigate whether the chemical and physical qualities of a carbonate rock are acceptable for further enhancement in the downstream sectors. This sample represents the potential of rock. While several research have examined carbonate rock as a potential in industrial raw material, the study of Perlis carbonate rock has grown more intriguing. Through this experiment, it is anticipated that the industrial potential of Perlis carbonate rock will be better understood, allowing a larger-scale experiment to be created.

Glass is an inorganic solid substance composed of silica sand, calcium carbonate, and sodium carbonate. Glass is a versatile material that may be shaped, colored, and patterned to resemble real crystal. Glass has been fashioned into utilitarian and ornamental things since antiquity, and it remains vital in uses as diverse as construction, housewares, and telecommunications, etc. Since dolomite and limestone have the same chemical makeup, researchers are examining the possibility of substituting limestone with dolomite in the manufacturing of glass.

The downstream industries are those that grow from the primary industry. The downstream products derived from the carbonate mineral are not yet employed by humans. Numerous companies utilize carbonate rock as a raw material for their products, such as fertilizer, which may lower the acidity of soil and is an agriculture product for plant and animal life. People are still unaware of carbonate potential as a primary component in downstream industries. The purpose of this study is to identify the by-product of carbonate rock materials.

Carbonate rock appears to have tremendous potential to contribute to the downstream and glass sectors, which will have a substantial positive impact on the economic and environment of Perlis. To accomplish this, local carbonate rock from Perlis State were prepared and characterized in terms of their properties using a variety of analytical techniques, including X-ray fluorescence (XRF), thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier transform infrared absorption spectra (FTIR), and physical properties analysis.

1.2 Problem statement

Carbonate rock deposits are usually discovered alongside limestones. This characteristic, along with the presence of varying levels of impurities like silica (SiO_2), sulphur (S), iron oxides, and alumina (Al_2O_3), has a significant impact on the acceptability of rock for certain applications. Carbonate rock is classified as a construction material, and it has a variety of applications. One of its most common applications is in construction, where it can be used in place of limestone. It is an essential raw ingredient for numerous industries, including iron and steel, ferro-alloys, glass, fertilizer, and many more. Carbonate rock chips are also utilized in the production of flooring tiles. Carbonate rock is prized primarily for its Mg content such as dolomite in some applications, and chemical composition is critical. Chemical characteristics (or degree of whiteness) are significant in several other applications. MgO concentration is commonly expressed following calcination (removal of CO_2). However, for control purposes, the glass industry often uses pre-calcined MgO content, with a theoretical maximum of roughly 21.8% MgO. Dolomite is a low-value product that does not lend itself to extensive transport distances when utilised in building. This is not the case with high-quality industrial dolomite. In glass making industry, the iron content of dolomite is considered as serious impurity since it affects the manufacture of colorless glass (Satyendra, 2017). Then the characteristic of the Perlis carbonate rock will be investigated to match the suitability percentage Mg content, impurities for the downstream industries.

1.3 Research objective

- To study and identify the physical, chemical characteristic for the natural and calcined Perlis carbonate rock such as dolomite for its suitability for the downstream industries.
- To determine the potential of the Perlis carbonate rock such as dolomite for the downstream industries.

1.4 Outline of the thesis

1.4.1 Chapter 1: Introduction

In the first chapter, the purpose of study is to determine the characteristic of Perlis dolomite for the glass and downstream industries. The significance is addressed by discussing the study based on the physical and chemical characteristics of the dolomite for the industries. This study can be contributed to the industries and made the dolomites minerals become more potential for the industries to use the mineral as a component in their product.

1.4.2 Chapter 2: Review of the Literature

This chapter will elaborate on the theoretical framework suggested by the study's goal. Thus, the literature review discusses and evaluates prior research on the subject. This chapter should not, however, solely summarize the findings of previous studies. Rather, a discussion and analysis of the corpus of information to determine what is known and what is not known about the issue. This conclusion generates research questions and/or hypotheses. In some instances, it may be necessary to replicate past studies.

1.4.3 Chapter 3: Methodology

This chapter outlines and defends the manner of data collection employed. This chapter also describes the data analysis methodology. Begin by detailing the approach used and how it was the most suitable option. Next, each stage and technique of the data collection and analysis process are described in depth. Although this part varies according on the selected approach and analytic technique, many of the following topics are frequently covered: (1) description of study methodology, internal and external validity (2) description of the population as well as a description and justification of the sample type or method used to pick units of observation. (3) development of instrument or technique for making observations (e.g., question guide, content analysis categories); pre-test reliability and validity of instrument or method; (4) Data coding; (5)description of data analysis; and (6)identification of themes and categories (qualitative or historical research)

1.4.4 Chapter 4: Result and Discussion

This chapter discusses the outcomes of data analysis and their significance in respect to the relevant body of theoretical knowledge. This chapter contains no discussion of additional study outcomes. All numerical information should be shown and summarized using tables and/or graphics. This chapter may be the most significant since it addresses the question "So what?" This chapter should also discuss the implications of the results for the researched issue.

1.4.5 Chapter 5: Conclusion

A conclusion is an essential component of a paper; it offers closure for the reader and reminds him or her of the document's contents and significance. This is accomplished by stepping back from the intricacies to examine the paper. In other words, it is a reminder of the central point. In most course papers, the conclusion consists of a single paragraph that simply and concisely restates the primary ideas and arguments, tying everything together to clarify the paper's thesis. Instead of introducing new ideas, a conclusion should clarify the purpose and significance of the paper. It may also offer suggestions for further study on the subject.

CHAPTER 2

LITERATURE REVIEW

2.1 General geology

Dolomite is a common rock-forming mineral. The chemical formula for calcium magnesium carbonate is $CaMg(CO_3)_2$. It is the primary component of sedimentary dolostone and metamorphic dolomitic marble. Dolomitic limestone is limestone that contains some magnesium. Dolomite is rare in the current sedimentary environment, although dolostones are prevalent throughout the geological record. They can range in thickness from hundreds to thousands of feet and represent a vast geographical region. Most dolomite-rich rocks were first deposited as calcium carbonate muds, which were later transformed into dolomite by magnesium-rich pore water. It is commonly associated with barite, fluorite, pyrite, chalcopyrite, galena, and sphalerite.

The structure of dolomite is like calcite, except every other cation layer contains magnesium ions instead of calcium ions. As a result, the ideal dolomite structure should include layers of calcium, magnesium, CO_3. Dolomites have the same potential to show order-disorder relationships as potassium feldspars. This is due to the possibility that part of the cation layers' purity is poor. For instance, some layers of calcium may include magnesium, while some layers of magnesium may contain calcium.

2.2 Introduction

Carbonate rocks are a group of sedimentary rocks made of carbonate minerals in most situations. Carbonate are sedimentary rocks formed at (or near) the Earth's crust by precipitation of carbon dioxide at crustal temperatures. Based on the Table 2.1, the principal types include limestone, composed of calcite or aragonite (unique crystal forms of $CaCO_3$), and dolostone, composed of the mineral dolomite ($CaMg(CO_2)$) and other types of rock that do not associate with calcium such as magnesite ($MgCO_3$) and siderite ($FeCO_3$). Carbonate rocks are the world's most depositional simple yet genetically most complex rocks. Some carbonate minerals can be formed by the combination of one or more ions with the CO_3^{2-} ion. Dolomite is an anhydrous carbonate mineral consisting mostly of calcium magnesium carbonate, $CaMg(CO_3)_2$. The term is also applied to sedimentary carbonate rocks generally made of the mineral dolomite. Dolostone is occasionally used as an alternate name for dolomitic rock. Dolomite is an unusual carbonate mineral. It is a widespread occurrence in historical platform carbonates but quite rare in Holocene sediments.

Table 2.1 Types of carbonate minerals

Mineral name	Chemical formula
Calcite	$CaCO_3$
Aragonite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Ankerite	$CaFe(CO_3)_2$
Magnesite	$MgCO_3$
Siderite	$FeCO_3$

2.2.1 Geological setting

Chuping Limestone of Malaysia is very well-known for its pure calcitic massive limestone with a diverse fossil species. It is exposed mainly in the North-western part of Malaysia namely in Perlis and Langkawi. It was named by Jones after the Chuping Hill in Perlis and was included as a part of Kodiang Formation as it resembles the basal part of Chuping Formation in Perlis after the discovery of Triassic conodonts by Ishii and Nogami in 1966. However, in 1975, de Coo and Smith had separated these two formations into two different stratigraphic units claiming that they are composed of completely different lithologies. The Chuping Formation is exposed mainly in the north-western part of the Malay Peninsula, especially in Perlis and Langkawi. In Perlis it was found overlying the Kubang Pasu Formation at Bukit Tengku Lembu, Bukit Wang Pisang, Bukit Manek and Bukit Chondong. It also forms several small hills namely Bukit Mata Ayer, Bukit Chabang, Bukit Tok Sami, Bukit Termiang, Bukit Tau, Bukit Guar Sami, Bukit Jerneh, Bukit Keteri, Bukit Panggos and Bukit Ngolong. These hills are aligned in two parallel belts side by side in a North-South direction stretching from the Southern Thailand, in which it was known as the Ratburi Limestone, to North Kedah forming prominent karst topography. The Chuping Limestone is made up of massive and unfossiliferous limestone meanwhile the base consists of well-bedded dark limestone with chert nodules and abundant fossils [6]. The age of Chuping Formation is estimated as Early Permian to Late Triassic by Kobayashi and Tamura. This is supported by the discoveries of several fossils such as *Marginifera* and *Hamletella* at Bukit Tungku Lembu, *Bellerophon, Euomphalus, Composita* and *Sinoporadendroides*. Fontaine et al. recorded the presence of *Hemigordiopsids, Sphairionia,* and *Lophophyllidium* at Bukit Wang Pisang. The most abundant fossil fauna was found at Bukit Merah which consists of red algae, *Tubiphytes, Globivalvulina, Pachyphloia, Langella, Lasiodiscus, Nodosariids, Pseudovermiporella nipponica*, rare bryozoans, *Sinoporaasiatica*. These fossils assemblages suggest that the Chuping Limestone was deposited on a sheltered shelf away from shoreline. Meanwhile isotopic data obtained from Chuping Limestone in Langkawi by Rao suggested that the carbonates were formed in a cool temperate shallow marine setting. (Noorhashima et al., 2013)

2.2.2 Mineralogy

Dolomite is also a rhombohedral carbonate with a structure that is a derivative of the calcite structure are shown in the Figure 2.1. The dolomite structure consists of alternating layers of Mg^{2+} and Ca^{2+} interspersed with CO_3^2 groups oriented normal to the c-axis. The alternation of Ca and Mg violates the c-glide plane in the calcite structure, giving the dolomite structure R3 space group symmetry. The CO_3^2 groups in dolomite are ordered as in calcite, with each metal cation coordinated by six oxygen atoms. However, in the dolomite structure, the charge density difference between Ca^{2+} and Mg^{2+} (due to the large difference in ionic radii results in a shift of the oxygen atoms towards the Mg^{2+} plane. The difference between the Ca-O and the Mg-O bond lengths in dolomite is 2.38 °A and 2.08 °A, respectively. This shift also violates the c-glide plane. (Gregg et al., 2015)

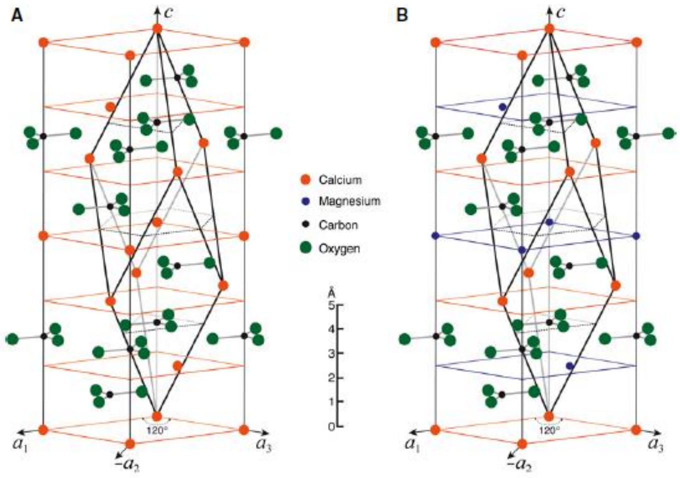

Figure 2.1 (A) The calcite hexagonal unit cell superimposed onto the rhombohedral unit cell. Planes of Ca2+ cations alternate with CO_3^{2} groups perpendicular to the c-axis. (B) The dolomite hexagonal unit cell superimposed onto the rhombohedral unit cell. Note that dolomite displays cation ordering consisting of alternating planes of Ca^{2+}, CO_3^{2} , Mg^{2+} and CO_3^{2} oriented perpendicular to the c-axis (Gregg et al., 2015)

2.2.3 **Properties**

The properties of dolomite that are useful for identification are presented in the Table 2.2 (Satyendra, 2017).

Table 2.2 Properties of Dolomite

No.	Item	Characteristics/properties
1	Category	Carbonate minerals
2	Chemical formula	$CaMg(CO_3)_2$
3	Chemical composition	Calcium – 21.73 %, Magnesium – 13.18 %, Carbon – 13.03 % and Oxygen – 52.06 %
4	Molecular weight	184.4 grams/mol
5	Rock Type	Igneous, Sedimentary, Metamorphic
6	Strunz classification	5.AB.10

7	Colour	Colourless, white, gray, peach, pink, yellow, and orange. Rarely yellow, green, red, and black.
8	Specific gravity	2.8–2.9
9	Bulk density of dolomite chips	Around 0.9 ton/cum
10	Melting point	More than 2600 deg C
11	Mohs Hardness	3.5 to 4
12	Streak	White
13	Luster	Vitreous to pearly
14	Fracture	Conchoidal
15	Tenacity	Brittle
16	Transparency or diaphaneity	Transparent to translucent
17	Crystal system	Hexagonal
18	Crystal forms and aggregates	Common in groups of small rhombohedral crystals, often with curved, saddle-like faces. Also prismatic, (although usually slightly curved), grainy, botryoidal, coxcomb, and massive. Uncommon in large rhombohedrons or rhombohedral aggregates.
19	Twinning	Common as simple contact twins
20	Solubility	Effervesces in hydrochloric acid. Slowly dissolves in nitric acid and hydrochloric acids.
21	Other characteristics	Occasionally fluorescent bluish-white or pink in shortwave ultraviolet light.

Dolomite is very similar to the mineral calcite. Calcite is composed of calcium carbonate ($CaCO_3$), while dolomite is a calcium magnesium carbonate ($CaMg(CO_3)_2$).

These two minerals are one of the most common pairs to present a mineral identification in field.

The best way to tell these minerals apart is to consider their hardness and acid reaction. Calcite has a hardness of 3, while dolomite is slightly harder at 3.5 to 4. Calcite is also strongly reactive with cold hydrochloric acid, while dolomite will effervesce weakly with cold hydrochloric acid.

Ferrous iron frequently replaces part of the magnesium in dolomite, and a full series exists between dolomite and ankerite [$CaFe(CO_3)_2$]. Manganese may also be used to replace magnesium, although only to a small amount and usually in conjunction with iron. Other cations known to substitute, albeit in low proportions, within the dolomite structure include barium and lead for calcium, and zinc and cobalt for magnesium.

Dolomite occurs in a solid solution series with ankerite ($CaFe(CO_3)_2$). When small amounts of iron are present, the dolomite has a yellowish to brownish colour. Dolomite and ankerite are isostructural. Kutnahorite ($CaMn(CO_3)_2$) also occurs in solid solution with dolomite. When small amounts of manganese are present, the dolomite will be coloured in shades of pink. Kutnahorite and dolomite are isostructural. (Hobart)

2.2.4 Analysis

Surface morphology of pure dolomite were characterized by using SEM. The micrographs of the dolomite will clearly illustrate the different particle size of pure dolomite powder. Pure dolomite that from Perlis Dolomite Industries contains wide range of particle size and thus sieving was carried out to obtain uniform particle size. The initial dolomite powders are in block-like shape with clear edges. (Fatimah, 2021)

The X-ray diffraction analysis of dolomite contains mineral dolomite ($CaCO_3.MgCO_3$), calcite ($CaCO_3$) and some impurities such as hematite (Fe_2O_3) and feldspar (silica minerals). For the natural dolomite, the diffraction peaks clearly observed at 31.5, 41.07, 44.8, 50.5 and 51.0 which correspond approximately to the 30.93, 41.12, 44.95 and 50.52 respectively for the standard. The dolomite was calcined at 6 hours with different temperature varied from 400 °C to 1000 °C. After calcination at 400 °C and 600 °C, there were no obvious change on its XRD patterns compared with that of natural dolomite. Obviously, there would be no significant decomposition of dolomite at this temperature. However, for the XRD patterns of dolomite calcined at higher temperatures, the peaks shifted were detected at 29.9, 43.5, 47.5 and 50.5 were corresponding to the calcium oxide. Meanwhile, the peaks at 34.0, 43.5 and 48.5 were observed that contributed to the magnesium oxide. Moreover, the crystallinity of CaO and MgO at 800 and 1000 °C was much stronger than that of dolomite at 400 and 600 °C. It indicates that at high temperature, the crystallization was further occurred. Besides, Mandrino et al. found that the thermal treatment under 700 °C had a small influence on the dolomite characteristics compared to the natural dolomite. (Fatimah, 2021)

FTIR analysis of the pure dolomite and calcined dolomite. The spectrum of natural dolomite showed two peaks at 717.68 and 873.26 cm^{-1}. The peak at 717.68 cm^{-1} was represented to the bending mode of CO_3. Later, the peak at 873.26 cm^{-1} was significant to the carbonate bending mode. However, when the temperature up to 800 °C, the dolomite decomposed to oxides of calcium and magnesium. Moreover, the FTIR spectra of CaO and MgO were shown as increasing the temperature. In addition, a little amount of adsorbed surface water was also observed in the FTIR spectra by the presence of the broad OH stretching of hydrated carbonate at 3218.34 cm^{-1}. The FTIR spectra for dolomites with different temperature varied form 400 °C, 600 °C, 800 °C and 1000 °C. The peak at 1421.09 cm^{-1} were clearly appeared show the structural transformation of natural dolomite to calcium and magnesium oxides. However, after calcination, the band at 1416.15 cm^{-1} at 400 °C was shifts to 1404.66 cm^{-1} due to the presence of calcium and magnesium oxides. Moreover, strong, and intense bands are observed at 3632.23 and 3690.98 cm^{-1} (800 °C), and 3694.03 and 3633.60 cm^{-1} (1000 °C) due to the calcium oxide. In addition, the weak bands at 868.70 – 865.76 were observed in all calcination dolomite. The weak bands at 865.76 and 1074.50 cm^{-1} in 1000 °C combine to form a strong and broad band after calcination process thus introducing to the effect of impurities such as silicates on the dolomite structure. (Fatimah, 2021)

For the chemical test using acidic and alkali solution for the dolomite the results for the reaction high-Mg calcite, blue precipitate is evident (indicates a carbonate high in available MgO). The intensity of the blue colour will decrease with MgO content. Low-Mg calcite, violet colour indicates a carbonate with no MgO. Dolomite, yellow colour (seen when no reaction occurs after etching and alkali solution is applied). As a blue coloration will be evident on evaporation of the alkali solution, observations must be noted within the first minute of application. Shield the test area from direct sunlight while undertaking this technique to avoid the loss of staining solution through evaporation and detect light colour hues of the precipitates. (Green, 2001).

2.2.5 Classification

Based on the weight percentages of calcite and dolomite within the overall carbonate part, four distinct varieties of limestone may be distinguished. They are presented in order of increasing dolomite content and decreasing calcite content below in Figure 2.2.

Calcite limestone: Calcite > 90%, dolomite < 10%.

Dolomitic limestone: Calcite 50–90%, dolomite 10%–50%.

Calcitic dolomite: Calcite 10%–50%, dolomite 50%–90%.

Dolomite: Calcite < 10%, dolomite > 90%.

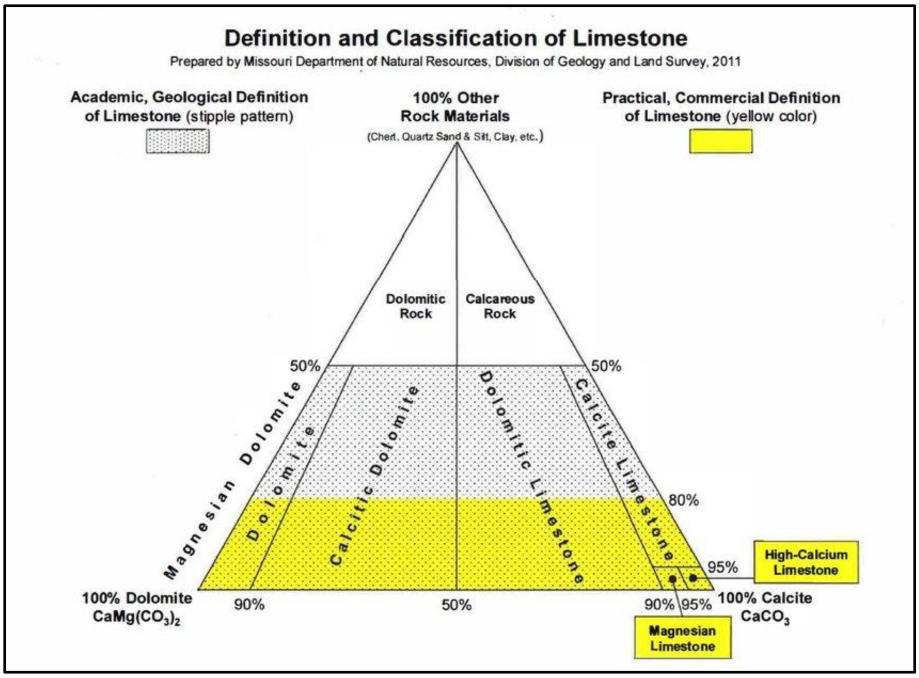

Figure 2.2 Classification of dolomite

2.3 Decomposition

Understanding of kinetics Important to the calcination process in industrial production is the heat breakdown of minerals. Due to their technical significance and theoretical intrigue, the kinetics of dolomite's thermal breakdown have been researched. Samtani et al. reported that the first stage of dolomite’s decomposition in the atmosphere of carbon dioxide occurs by a formation of an unstable magnesium carbonate which decomposes immediately to the magnesium oxide and calcium carbonate (half-burnt dolomite). The second stage of dolomite’s decomposition involves the reversible dissociation of calcium carbonate to calcium oxide which is a highly reactive. Subsequently, calcium oxide probably undergoes carbonation and hydroxylation with carbon dioxide and moisture from air. Caceres suggested that severe grinding of dolomite causes mechanically induced crystal structure’s distortion and the existence of two different Mg forms namely Mg-I and Mg-II. Decomposition of Mg-II takes place at temperatures lower than 893 K, whereas temperatures greater than 993 K are required for the decomposition of Mg-I. Structurally deformed dolomite crystallites developed due to mechanical treatment decompose in two stages at a higher and lower CO_2 partial pressure. Barcina et al. reported that DTG curves in nitrogen atmosphere of quarry dolomites show two peaks (not perfectly resolved) at 1,023 and 1,073 K and that the MgO formation is not completed when the $CaCO_3$ decomposition starts. These authors reported that mixed oxides of Ca and Mg did not form because of the calcination. According to Barcina et al. a smaller size of magnesium with respect to calcium atoms facilitates the magnesium mobility, and thus the formation of carbon dioxide associated to magnesium oxide is kinetically favored against the formation of CO_2 associated to calcium dioxide. The decomposition mechanism of dolomite is the source of many controversies. There is no agreement between these studies concerning the kinetic model, the influence of CO_2 pressure, and the rate-controlling step. Gallai et al. studied the mechanisms of growth of MgO and $CaCO_3$ during the dolomite partial decomposition under CO_2 pressure of 0.02–0.5 atm. They reported that the decomposition rate is limited by the diffusion of Mg from $CaCO_3$/MgO interface to MgO/CO_2 interface. Fine particles of MgO are formed at the surface of the initial dolomite needles. MgO grows with an external development, while the calcium carbonate develops inward at the dolomite phase. Growths of MgO and $CaCO_3$ can be controlled by the diffusion of magnesium through the MgO-phase surface. (Olszak-Humienik et al., 2015)

2.4 Uses of carbonate rock

2.4.1 Downstream industries

CaO and MgO play the role of network modifiers in the glass making process, which makes dolomite a very important mineral. The glass industry requires high-quality dolomite with the least amount of iron and silica feasible. Dolomite of glass quality is characterized by its purity and uniformity. Dolomite is a calcium-magnesium carbonate compound ($CaCO_3$, $MgCO_3$). Iron, chromite, manganese, vanadium, and lead are the most prevalent impurities that can produce flaws in float glass or colored glass. For certain commercial colorless glasses, a Fe_2O_3 percentage of up to 0.25 percent is acceptable, while for pure colorless glasses, a maximum Fe_2O_3 value of 0.04 percent is occasionally stipulated.

Dolomite is utilized to introduce lime and magnesium into the glass melt. Lime and magnesia both increase the durability of glass, but magnesia slows the devitrification process, which is essential for producing flat glass.

By far the largest portion of all industrially manufactured glass is soda lime glass. As the name implies, soda and lime, in addition to sand, are key components. The normal composition of soda lime glass is 10 to 15 percent CaO or CaO + MgO. In practice, soda lime glass is used to create beverage bottles, food jars, basic drinking glasses, and dinnerware. Limestone and dolomite provide the majority of the CaO and MgO required for glass production. Dolomite (MgO) has a good impact on both the melting process and the glass's characteristics.

2.4.1(a) Float glass

Most of the plate glass is created using float glass technique, in which the glass melt is passed over a bath of molten tin. This results in the production of extremely high-quality plate glass, which has several uses in the construction and automotive sectors. Colorless / low-iron plate glass is utilized in the production of solar modules and hence the generation of solar power. Plate glass is a crucial architectural element in contemporary architecture. In addition to limestone, up to 5 percent of dolomite derived MgO is added to the mixture for plate glass. This gives a high level of process stability, boosts the scratch resistance and chemical resistance of the glass, and improves the viscosity of the glass melt. The lower calcination temperature of $MgCO_3$ in dolomite and the creation of low-melting mixture phases also contribute to a decrease in energy consumption when dolomite is employed.

2.4.1(b) Container glass

Glass is important in food containers, beverage bottles, and pharmaceutical and cosmetic product containers. It is gas-tight, tasteless, and inert, providing excellent conditions for these containers. The unique form and hue of glass containers provide significant marketing benefits. Despite or since huge quantities of recycled glass are utilized in the manufacturing of container glass, high-quality, low-iron natural raw materials are required for glass production. In addition to limestone as a CaO carrier, it has been shown to be advantageous to employ between 1.8 and 3.4% MgO from dolomite in the manufacturing of container glass. The tendency of glass to crystallize can be minimized, as can the amount of soda and refining chemicals. MgO improves the cooling qualities of containers that are heavy and complicated in design.

2.4.1(c) Continuous Glass Fiber Filaments

Textile glass fibres are primarily utilised in the production of glass fiber-reinforced plastics (GRP). Transport (automotive, aircraft construction, shipbuilding) to wind power, electronics, and sports equipment use these plastics. The production of E-glass and ECR (E-Glass Chemical Resistant) glass for continuous glass fibres necessitates the use of exceptionally fine and high-quality raw materials. Utilized are finely milled limestone and dolomite products in addition to fine white lime and dolomite lime. Calcined lime and dolomite products, which are burned to make E-glass, C-glass, and ECR-glass, enhance the performance and capacity of glass melting tanks for glass fibres. Utilizing burned lime and dolomite lime in fully electrified cold-top glass melting tanks inhibits the creation of undesirable CO_2 foam layers and hot breakthrough in the batch blanket.

2.4.1(d) Technical glass

The field of technical glass includes TV and computer monitor glass, lighting glass (tubes and bulbs), optical glass, laboratory and technical glassware, borosilicate glass and ceramic glass (hotplates and high-temperature residential uses), and glass for the electronics sector (LCD panels). CaO and MgO perform a minor but crucial function, as other glass-forming oxides are typically used (boron, aluminium, etc.).

2.4.1(e) Glass fibre for insulation

Glass, mineral, and stone wool have been utilised to insulate against heat, cold, and noise for over sixty years. Mineral wool is comprised of natural and regional raw resources, such as silica sand or basalt, as well as the eco-friendly utilisation of recycled glass. It is the insulation material of choice in building and industries. The fibres of glass or stone wool are formed by forcing compressed air through a stream of glass or by spinning. The addition of limestone and dolomite adjusts and influences the desirable qualities of the melt and fibres. Lime and dolomite products, depending on their composition, serve as fluxing and stabilising agents for glass.

2.4.1(f) Construction

Dolostone is most used in the building sector. It is crushed and sized for use as road base, aggregate in concrete and asphalt, railroad ballast, riprap, or fill. In addition to being calcined in the manufacturing of cement, dimension stone is also carved into blocks of precise dimensions.

2.4.1(g) Chemicals

The interaction of dolomite with acid also makes it helpful. It is utilized in the chemical industry for acid neutralization, in stream restoration projects, and as a soil conditioner. Organic chemistry relates to the petroleum industry, which predominantly employs lime products as reagents for chemical synthesis. Compared to other alkaline, such as caustic soda, lime's pricing is competitive and reliable (NaOH). In inorganic chemistry, mineral substances are processed. In this industry, lime products are predominantly employed as neutralizing and cleaning reagents in chemical synthesis.

Para-chemistry is the transformation of fundamental chemicals into useful substances. Lime products are used in processes as chemical reagents and neutralizing agents.

2.4.1(h) Agriculture

Limestone, and dolomite are utilised in agriculture and forestry as a source of magnesia (MgO) for a feed ingredient for animals and to rectify soil acidity. These minerals are necessary for healthy plant development and agricultural production enhancement. This improves land utilisation and reduces the environmental effect of intensive agriculture (fertilisers), such as groundwater contamination.

2.4.1(i) Steel making

Quicklime is an essential active ingredient for removing silica and phosphorus from converters and electric arc furnaces. After absorbing impurities, lime generates a basic slag more rapidly. Lime of high grade creates slag of excellent quality that is ecologically benign and simple to manage and treat. Dolime increases the longevity of converter refractory linings. Additionally, it shields them from the corrosive effects of some impurities present in heated metals. The addition of dolime causes MgO to dissolve in the slag. This gives an exceptional capability for buffering. Excess MgO safeguards refractories and tap holes, minimising the need for gunning and repairs.

2.4.1(j) Ceramics

Limestone minerals are necessary for the manufacturing of ceramic products, such as sanitary ware, porcelain floor and wall tiles, porcelain figurines, and other fired ceramic items. One of the two major components of a ceramic body is ball clay. It is essential to the production of "green strength" or "flexibility." It also serves to bind other components and promotes uniform fire in the kiln. In certain ceramic applications, such as the manufacture of wall tiles, limestone is employed as a fluxing agent and to provide porosity.

2.4.1(k) Refractories

When dolomite is calcined at extremely high temperatures, sinter dolomite is created. It can be used as a granular refractory compound to repair linings. It can be moulded into bricks that fit into cement kilns and casting ladles' refractory linings. For instance, using dolime rather than pure quicklime in the steel-refining process increases the lifespan of the refractory linings. Dolime addition causes the slag to contain MgO in solution. Excellent coating protection and remarkable buffering capability are guaranteed by MgO particles in suspension. MgO precipitates in excess, shielding tap holes and refractories. As a result, less gunning and maintenance is required.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter gives an outline of research methods that were followed in the study. Methodology is a systematic way to find out the result of a given problem. It defined as the study of methods by which knowledge is gain and its aim is to give the work plan of the research. The selection of research methodology is based on the research objective, the nature of information and the resources available on how to characterize the sample so that it will be useful for the glass and downstream industries.

The characterization of the sample will undergo several stages. Because of the sample require get in the form of solid rock, the sample will undergo several steps of crusher. The first one is the jaw crusher then goes to the cone crusher and finally go to the ring mill or agate mortar to get the sample in form of powder. Not all the sample will in the form of powder because there is certain experiment that required the sample in the form of small solid rock.

The methodology will be divided into three steps, to identify the mineralogy of sample, chemical composition or analysis of the sample and the thermal treatment of the sample. By doing this the properties of the samples may be known whether the sample suitable for the glass industries and the downstream industries.