SHORT PERIOD OF STUDY ON THE POREWALL STABILITY OF CARBONATE ROCK IN PERAK

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CERTIFICATION OF APPROVAL

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A project interim submitted to the
Petroleum Engineering & Geoscience Department
UniversitiTeknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(PETROLEUM ENGINEERING)

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PERAK, MALAYSIA

April 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified source or persons.

CHARLES CALVIN TING FONG YUH

Abstract

There is a gap of knowledge on the dissolution kinetics of carbonaterocks originating from Malaysia. This information is critical for CO2 sequestration and EOR endeavours. Samples of carbonate rocks were taken from SimpangPulai and Sungai Siput area of Perak, Malaysia. Theobjective of this study was to evaluate the kinetics of dissolution of these carbonate rocks using two types of acids namely hydrochloric and acetic acid. These acids represent inorganic and organic acids respectively.

Low concentration of 0.01M was used to simulate [H+]concentrations in CO2 sequestration situations. The low concentration ofacid also enables us to better understand the dissolution rates of thecarbonate rocks. The experiments were done at room temperature. Thisapproach also enables us to better understand the change in the strengthof the carbonate rock after acid dissolution. Porosity and permeabilitychanges were recorded intermittently. The preliminary results show thatdissolution kinetics is dependent on the resident fabric of the rock andthe type of complexation ions present. Re-precipitation of carbonateminerals was not observed during the experiments.

ACKNOWLEDGEMENT

During the course of this project, I would like to thank my supervisor Dr.EswaranPadmanabhan for his guidance and motivation to start and complete this project. Also special thanks to GA Syamim and Yasser for helping in conducting some of the experiment since the lab technicians are not available. I would also like to thank the lab technicians in UTP for allowing me to use the lab throughout the period of the project.

Special appreciation for Mr Saw Lid Haw the Quarry Manager of Omya Malaysia for allowing me to collect rock samples for this project.

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1.0 Introduction

1.1 Background of Study

Carbonate rocks are part of sedimentary rocks that are formed in marine environments via compaction, cementation and dolomitization processes on its sediments. Due to its main chemical composition of calcium carbonate, $CaCO_3$ it is easily dissolved when exposed to acidic solution. This occurrence can be widely seen in the formation of caves which are formed as limestone formation slowly reacts with the low acid content in underground water that seeps through. However, the rate of dissolution of carbonate rock varies widely according to the type of geochemical processes that the carbonate rock has undergone.

This is because its crystal structure maybe altered under high pressure and temperature environment when it is in contact with lava or when it is chemically changed when it is being replaced with more stable minerals when it is dissolved by underground water. The precipitation of cements from minerals that are trapped in its empty pore spaces will also affects its dissolution rate when exposed to acidic solution.

Due to its tendencies to being dissolved by acidic solution, carbonate rocks has high porosity. However, the pores are not interconnected which makes it low in permeability. The high porosity in carbonate rock makes it a good candidate as a reservoir rock to contain hydrocarbon but the low permeability impedes the movement of the hydrocarbon from being produce from the wells drilled into the formation. Hence, acid stimulation methods such as matrix acidizing is suitable for naturally fractured carbonate reservoir to remove the formation damage near wellbore due to drilling, completion and scales blocking the fractures. Acid fracturing method is suitable for homogeneous carbonate reservoir in order to create linear flow of infinite conductivity along the fracture stimulated.

In terms of stability of physical structures of carbonate rocks such as caves which are important in Malaysia. Mulu cave and Niah cave in Sarawak are among the biggest caves in the world which are important in terms of economic value as both caves are tourist attraction. Moreover, Niah cave is also known for bird's nest industry as well as the natural fertilizer, guano which is the dropping of bats. In addition, both caves also carry important historical discoveries such as the existence of early civilization through the discovery of skeleton of early human civilization which dates back to thousands of years ago. Besides that, BatuCaves and Sam Poh Tong Cave are used as temples. These caves are under threats as it is being slowly dissolved by the acidic solution such as underground water or acid rain effects. The strength of the structure of these caves will be severely affected if the dissolution rate is much faster.

As such, the purpose of this paper is to better understand the kinetic dissolution of carbonate rocks which has undergone different geothermal conditions. The changes in terms of porosity and permeability and stability of the pore wall will be presented based on the test conducted on the sample carbonate rocks which has undergone the acid dissolution at room condition. The strength of the corroded carbonate rock sample will also be tested in order to see how acid dissolution of carbonate rock affects its physical strength.

1.1 Objectives

- To study the dissolution rate of the sample of carbonate rock that has undergone different geochemical conditions via samples from Sungai Siput and SimpangPulai using organic and mineral acid at different concentration under atmospheric conditions.
- To test the pore wall stability of the carbonate rock that has undergone significant acid dissolution in terms of its permeability and porosity and strength.

1.2 Problem Statement

1.2.1 Problem Identification

- Does the rate of dissolution of carbonate rocks differ for a particular acid?
- Does the rate of dissolution of carbonate rocks differ in different types of acid?
- Does the acid dissolution selective in terms of type of matrix within the limestone?

1.2.2 Significance of the Project

This project will enable us to better understand the difference in kinetic dissolution of the different carbonate rock samples in Perak. This understanding will enable us to better understand the factors that may contribute to the dissolution rate of the rock in acid. It will also enable us to know how the strength of the rock is affected by the acid dissolution.

1.3Scope of studies

- Acid dissolution rate of mineral and organic acids on carbonate rocks under atmospheric conditions
- Porosity and permeability of carbonate rock before and after undergoing acid dissolution
- Thermal conductivity of the different carbonate rock samples of SimpangPulai and Sungai Siput
- Mineral content identification of the carbonate rock samples taken

1.4 Relevancy of the Project

There has not been enough study done on the kinetic dissolution of carbonate rocks in Malaysia particularly in Perak area. A better understanding will enable us to better understand the rate as well to document the changes occurring within the rock particularly the surface in order to understand how the use of the type of acid have effect on its rate. This is particularly important for acid stimulation works in carbonate reservoirs.

1.5 Feasibility of the Project within the Scope and Time Frame

The project should be able to complete within the time limit given as it is for a study of short time scale only. As such it will be able to finish within the scope of study. However, the experiments will commence during the semester break as the lab and equipment will be available during that time as compared to during normal semester period.

2 Theory

2.1 Classification of Carbonate Rocks

Carbonate rocks are classified as a type of sedimentary rock which is formed through both chemical and biochemical processes. [1] There are many ways to classify carbonate rocks with various paper presented on it. However, the two most commonly used classification is by Folk (1959, 1962) [3, 4] and Dunham (1962) [5] which is based on the matrix content of the carbonate rock.

Folk [3, 4] introduces allochemical rocks concept (transported carbonate grains) for limestones containing more than 10% allochems. The rock is further subdivided into two groups based on the percentage of interstitial material: sparryallochemicallimestones (contains sparry calcite cement of clear coarsely crystalline mosaic calcite crystals) and microcrystalline allochemical limestone (contains microcrystalline calcite mud which is grayish or brownish subtranslucent particles less than 5 microns). Scholle& Ulmer-Scholle (2003) further subdivided the allochem ratios of Folk (1962). Folk classify rocks with appreciable matrix as micrites and matrix-free rocks with sparry calcite cement as sparites which are further classified based on its most common grains. Hence, this classification is suitable for **thin section study**.

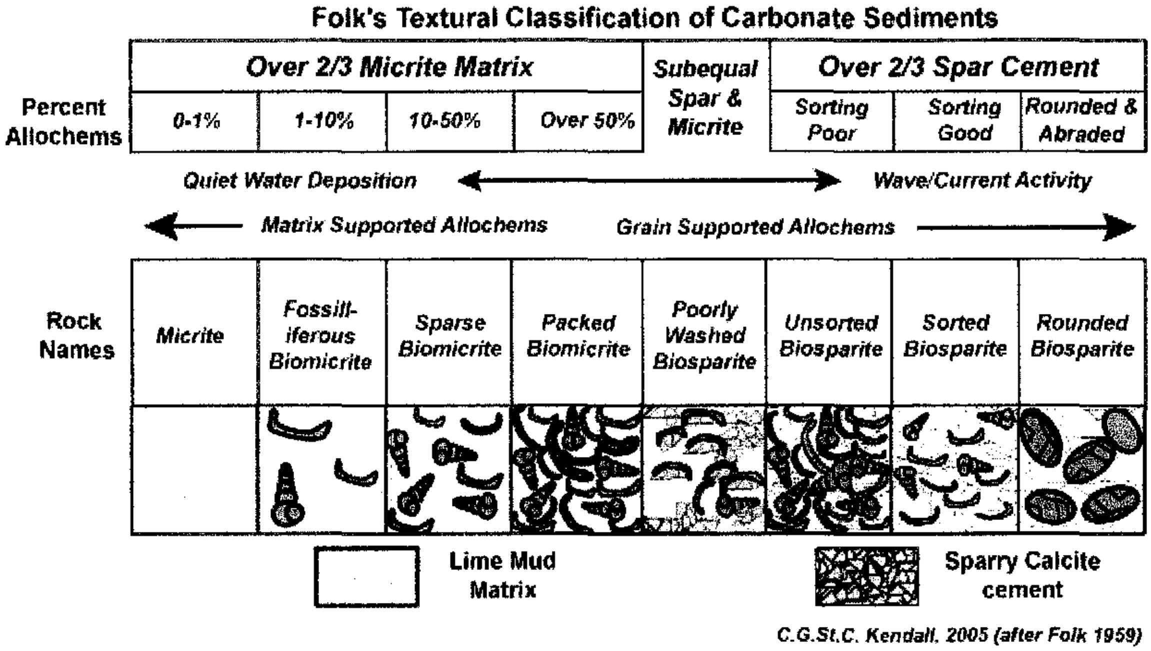
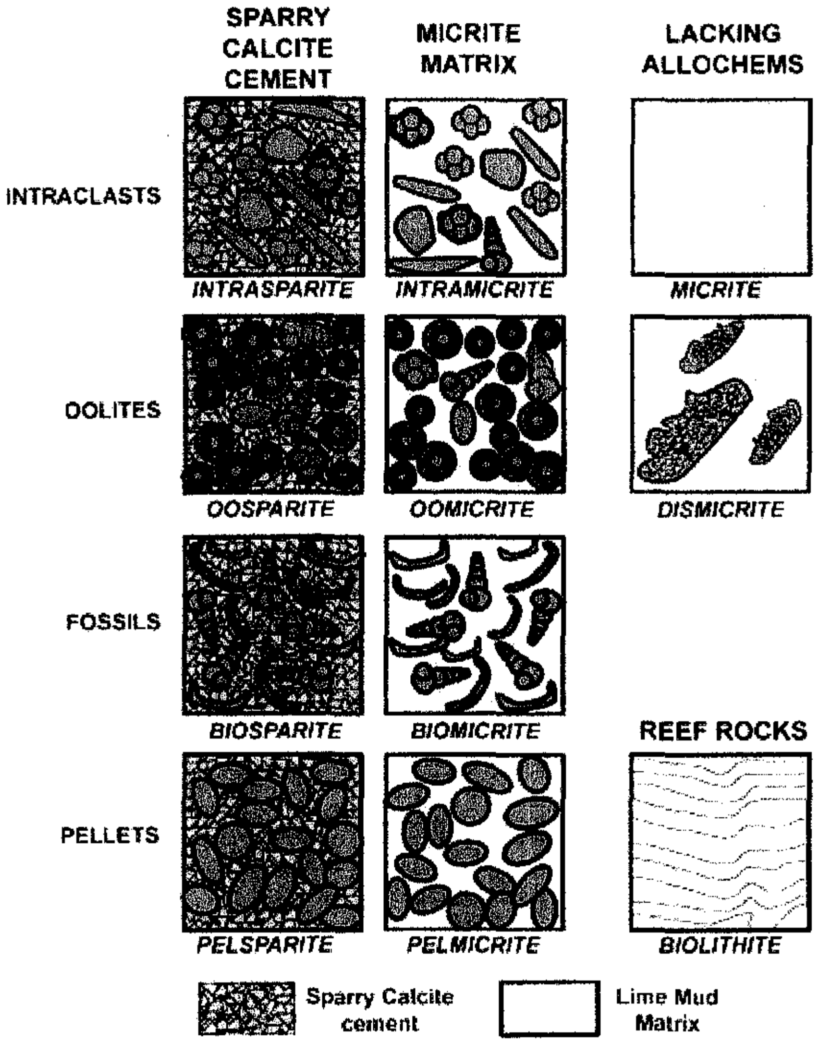
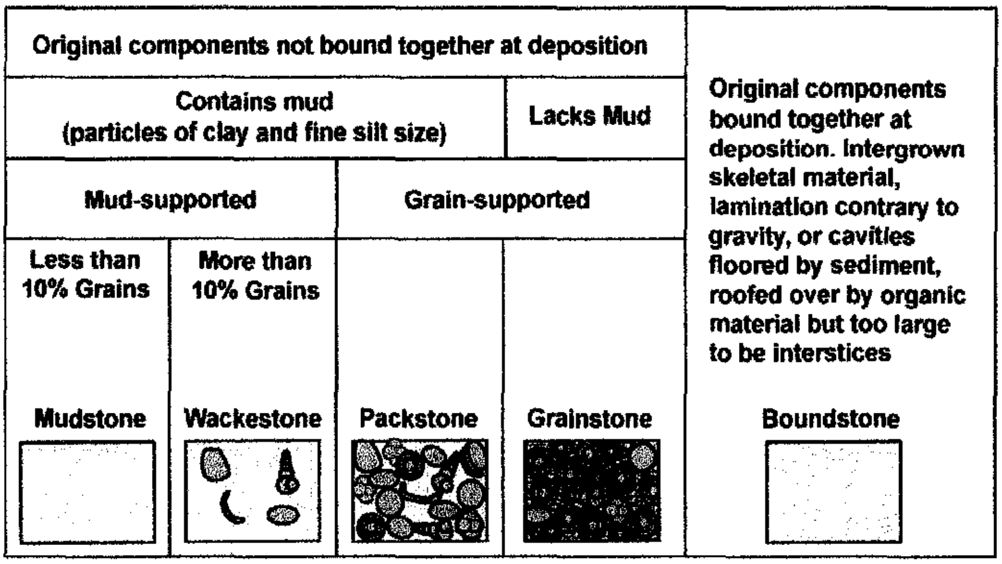


Figure 1.1 shows the Folk's textural classification of carbonate sediments and the rock names



C.G.St.C. Kendall, 2005 (after Folk 1959)

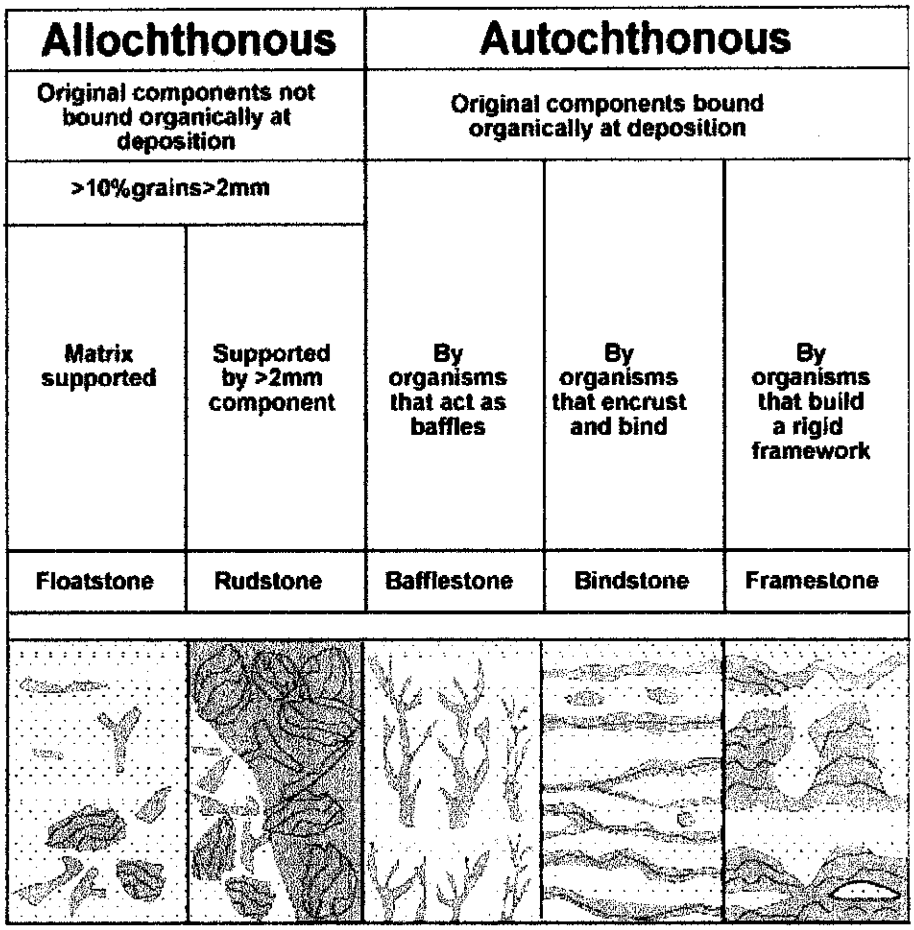
Figure 1.2 shows the carbonate rock classification by C.G.St.C. Kendall which is based on Folk'swork



C. G. St. C. Kendall, 2005 (after Dunham, 1962, AAPG Memoir 1)

Figure 1.3 C.G.St. C. Kendall's classification done after Dunham's work.

Meanwhile, **depositional texture** is the main focus of Dunham's [5] classification and its modification by Embry and Klovan (1971) [7] and James (1984) are suitable for rock descriptions that employ a hand lens or **binocular microscope** as shown below.



Allochthonous		Autochthonous		
Original components not bound organically at deposition		Original components bound organically at deposition		
>10%grains>2mm				
Matrix supported	Supported by >2mm component	By organisms that act as baffles	By organisms that encrust and bind	By organisms that build a rigid framework
Floatstone	Rudstone	Bafflestone	Bindstone	Framestone

Textural classification of reef limestones after Embry & Klovan (1971) and James (1984)

Figure 1.4 shows the textural classification of reef limestones after Embry and Klovan (1971) and James (1984)

2.2 Depositional environment of carbonate

Generally there are three types of past or present depositional environment for carbonate [6]:

- Ramp continental margins are gently sloping continental platform sloping toward the ocean (<1 degree). It is limited by the emerged continent and toward the oceanic basin by gentle continental break. Thus, an environment of high energy as the amplitude of the wave increases as the depth of the sea decreases.
- Rimmed margins are continental platform limited towards the ocean by a steep and abrupt continental break where a nearly continuous carbonate rim or barrier develops. The rims and barriers act as wave resistant structure made of coral reef (alive or dead)

and oolitic sand shoals. A low energy environment of 'lagoonal' found further landward from the rim or barrier which is characterised by grading landward into tidal flat. In present day, these places are colourful tourist snorkelling spots. The rim or barrier is a high-energy environment for oceanward. There is less living organism in this wavy and scummy environment.

- Isolated platforms or 'Bahama type' are shallow platform ranges from 10 to 100s km wide offshore of shallow continental shelves, surrounded by 100 to 1000m deep of water. Thus the environment is characterised by the absence of siliciclastic input.

2.3 Carbonate Mineralogy

There are three groups of carbonate rock namely calcite, dolomite and aragonite. A better understanding of the mineral content of the carbonate rock will help us in better understanding of dissolution rate of the core plug sample.

Calcite Group (hexagonal)		**Dolomite Group (hexagonal)**		**Aragonite Group (orthorhombic)**	
Mineral	Formula	Mineral	Formula	Mineral	Formula
Calcite	$CaCO_3$	Dolomite	$CaMg(CO_3)_2$	Aragonite	$CaCo_3$
Magnesite	$MgCO_3$	Ankerite	$Ca(Mg,Fe)(CO_3)_2$	Witherite	$BaCO_3$
Siderite	$FeCO_3$	Kutnohorite	$CaMn(CO_3)_2$	Strontianite	$SrCO_3$
Rhodochrosite	$MnCO_3$				

Table 1.1 above shows the mineralogy of three different types of Carbonate rock groups; namely Calcite, Dolomite and Arogonite [2]

2.4 Porosity and permeability of carbonate rocks

Raymond C. Murray, [16] in his paper entitled "Origin of Porosity in Carbonate Rocks" suggested the importance of analysis on the depositional and post depositional processes that took place in carbonate rocks. He further elaborated that "primary interparticle porosity is formed during deposition of a well sorted calcareous sand or gravel under the influence of strong currents or waves or by local production of calcareous sand size particles with sufficient rapidity to deposit particle on particle with little or no interstitial mud. Dissolution of interstitial mud in a calcareous sand can produce a microvuggy porosity resembling interparticle pore space." Meanwhile processes such as cementation by calcite, anhydrite, dolomite or quartz destroy porosity and pore size. Thus dissolution of nonreplaced limestone produces porosity.

Choquette& Pray (1970) [17] emphasised on the three major historical events in sedimentary carbonate which are important for dating its origin and modification of porosity, independent of lithification. The processes are:

1. Creation of sedimentary framework by clastic accumulation or accretionary precipitation (final deposition)
2. Passage of a deposit below the zone of major influence by processes related to and operating from the deposition surface
3. Passage of the sedimentary rock into the zone of influence by processes operating from an erosion surface (unconformity)

Final deposition enables recognition of predepositional, depositional and post depositional stages of porosity evolution. The end of final deposition time distinguishes the primary from the secondary porosity (postdepositional). Major changes in carbonate sedimentary rocks during postdepositional time occur near the surface at very early in burial history of at a certain stage associated with uplift and erosion. The porosity created or modified during these times can be differentiated through three major events:

1. Eogenetic (early burial stage)
2. Telegenetic (late stage)
3. Mesogenetic (normally very long intermediate stage)

There are fifteen basic porosity types where seven are abundant types (interparticle, intraparticle, intercrystal, moldic, fenestral, fracture and vug) and another eight are specialised types.

This involves processes such as:

1. Modification (solution, cementation and internal sedimentation)
2. Direction or stage of modification (enlarged, reduced or filled)
3. Time of porosity formation (primary, secondary, predepositonal, depositional, eogenetic, mesogenetic, and telegenetic).

Shafiee&ApostolosKantzas [18], works on measurement of pore architecture of carbonate reservoir using computerized tomography, CT scan enables the understanding of variation of pore architecture which is complicated due to the processes of precipitation, lithofication and diagenesis in carbonate rocks in analysing derived rock properties such as porosity, permeability and connectivity.

Generally, carbonate rock porosity ranges from 10%-30% which is fairly high compared to other types of rocks because of the dissolution process when it is exposed to acidic solution. However, due to the difference in dissolution rate of its chemical content, most of the pores are not interconnected, thus resulting in a low permeability of 1-10 milidarcies. Permeability is a measure of ease of flow of substance across the porous media like carbonate rock.

In this paper, the porosity and effective permeability of the carbonate rock sample will be conducted in the lab through core flooding using nitrogen gas at temperature and pressure of atmospheric and reservoir condition both before and after the acid dissolution experiment in order to compare the changes and also to see how the process differs both in exposed outcrop and also in reservoir conditions.

2.5 Dissolution kinetics of carbonate rock

The modified diffusion boundary layer (DBL) model explains the relation of the dissolution rate of dolomite with rotating speeds at conditions far from equilibrium through the technique of rotating disk experiment. In this experiment, the kinetics of dolomite dissolution in flowing CO_2-H_2O system using the rotating disk technique and catalyst. The solution used in this experiment is equilibrated with various CO_2 partial pressures (P_{CO2}) from 30 to 100 kPa.

Many studies have been done on kinetics and rate limiting mechanism for calcite dissolution compared to dolomite. Lund et al [11] studied the hydrochloric acid dissolution for dolomite to determine the conditions where rate is diffusion-limited or surface reaction-limited. Herman [12] conducted laboratory experiments on dissolution kinetics of dolomites with emphasis on understanding the effects of solvent motion and dissolution rates modified by carbonate lithology.

Meanwhile, Busenberg and Plummer [13] carried out extensive work on kinetics of dolomite dissolution at various temperatures and PCO2 where they obtained the Busenberg's equation for net rate of dissolution as

$R=k_1(aH^+)^n + k_2(aH_2CO_3)^n + k_3(aH_2O)^n - k_4(aHCO_3^-)$, where

K_1,k_2 and k_3 are forward rate constants, k_4 is the backward rate constant, and a refers to the activity. They have found that the exponent n is equal to 0.5 when temperatures are below 45°C.

Chou et al [14], made a comparative study on the kinetics and mechanisms of dissolution of carbonate minerals where they found that n= 0.75 for dolomite dissolution which indicates a more complex surface reaction as compared to calcite.

Liu &Dreybrodt [15] studied on the effects of CO2 conversion reaction in limiting the rates using the disk technique with introduction of carbonic anhydrase (CA) into the solution at various partial pressure of 30- 100 kPa. They found that initial dissolution of dolomite is 2.5-7.5 times lower than limestone where the difference increases at lower partial pressure. For limestone, CA increases the dissolution rate more than 10 times at high partial pressure more than 5 kPa compared to dolomite where CA influence the dissolution rate at low partial pressure of less than 5 kPa. This confirms the findings of Chou et al that dolomite dissolution is due to more complex surface reaction.

This dissolution kinetics experiment to be conducted in the lab for this research paper will be using organic and mineral acid solution of 0.01M that is used to react with the carbonate ions which are ionized when the carbonate rock is present in water. This will enable us to compare the difference between the acid dissolution of organic acid like acetic acid and mineral acid like hydrochloric acid on the dissolution kinetics of the carbonate rock.

The pH reading of the acid solution will be taken before the carbonate rock core sample is added into the solution. The pH reading of the acid solution should increase overtime as acid reacts with the carbonate ion from the carbonate rock sample. The pH reading is taken every hour for the first five hours of reaction as reaction is most likely to take place during this period. After that the pH reading is taken once a day at the atmospheric temperature for two weeks.

The chemical reaction for limestone and dolomite with hydrochloric acid, HCl are as below:

$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$ (limestone)

$CaMg(CO_3)_2 + 4HCl \longrightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2$ (dolomite)

The chemical reaction for limestone and dolomite with acetic acid, HC_3OOH are as below:

$CaCO_3 + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + CO_2$ (limestone)

$CaMg(CO_3)_2 + 4CH_3COOH \longrightarrow Ca(CH_3COO)_2 + Mg\,(CH_3COO)_2 + 2H_2O + 2CO_2$
(dolomite)

2.6 Thermal conductivity

Thermal conductivity is the property of a material to conduct heat which is measured in watts per kelvin per meter (W/K m). Thus, it measures the energy loss in watts per changes in temperature over an area with a certain thickness. This follows the Fourier's Law for heat conduction.

Zierfuss (1969) [19], in his research on carbonate rock conductivity found out that:

1. Heat conductivity decreases as porosity increases
2. Dolomite is a better heat conductor than limestone of the same porosity
3. Anhydrite (if comprising more than 5o percent of rock) causes extremely high heat conductivity values

Thomas Jr. et al (1973) [20] also found the same result as Zeirfuss. However, they also found out that water absorbed samples have greater thermal conductivities than air-saturated (dry) samples of the same rock.

3 Methodology

3.1 Project activities

3.1.1 Carbonate rock core plug preparation

A big slab of carbonate rock sample was taken from Sungai Siput which will be used for the experiment. The rock is cut into a slab of rock with a thickness of 20mm. It is then cut into smaller slabs with width of 12cm so that it can be fitted into the rock holder which will be used to hold the rock in tight grip during coring. Core plug of 1.5 inch diameter were prepared as sample for the acid dissolution to be used later.

Figure 1.5 shows the Sungai Siput carbonate rock slab of thickness 20mm. The right hand side portion of this rock is taken to be used in this experiment because the rock lithology is more consistent compared to the left hand side of the sample where complex structure (white lines).

Figure 1.6 shows the process of cutting the rock slab into smaller slabs of 12cm width using the rock cutter.

Figure 1.7shows the 12 cm width rock slab cross section after being cut.

Figure 1.8 shows the Corex machine that will be used to make core plug of 1.5 in diameter

Figure 1.9 shows the core plug samples of 1.5 inch diameter that has been prepared

Figure 1.10above shows the Geo cutter that is being used to smoothen the surface of the core plug especially the edges of the core plug.

Thin sections of the carbonate rock sample have also been prepared using the leftover rock used for coring previously.

Figure 1.11 shows the Micracut 175 which is being used to cut thin section sample.

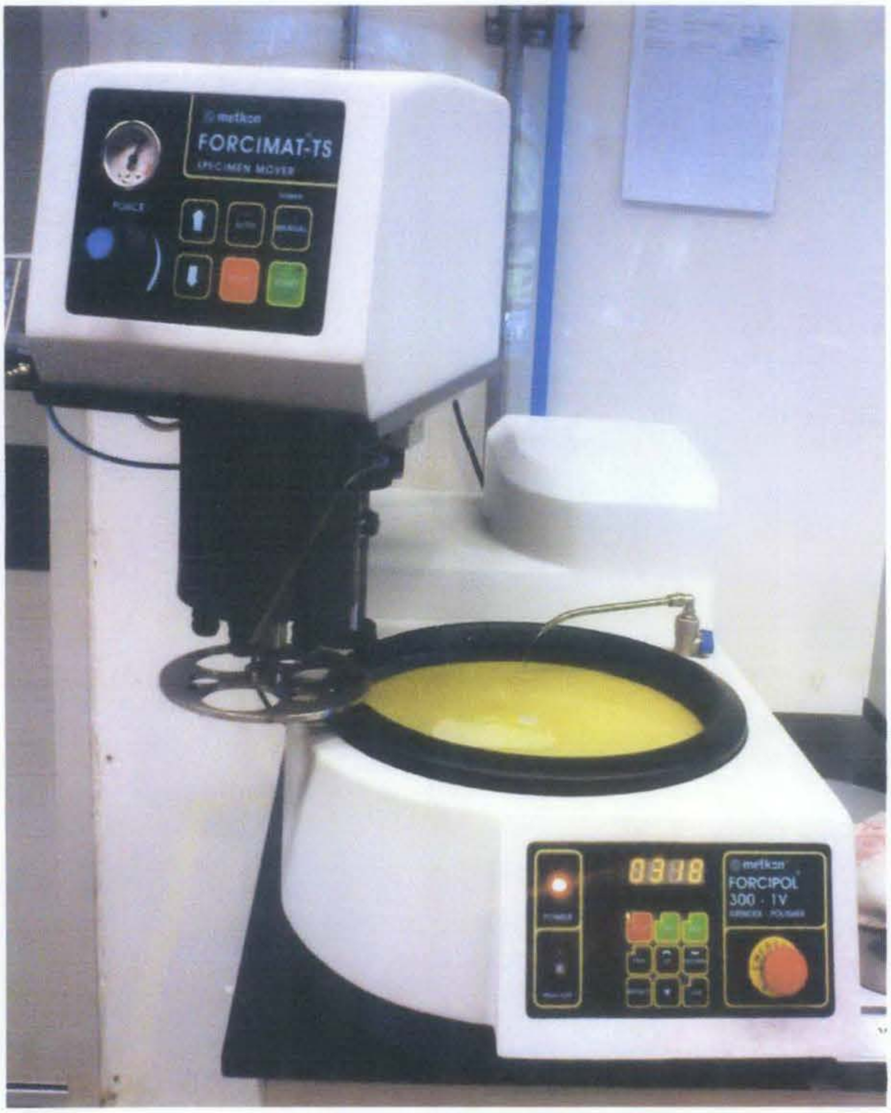


Figure 1.12 shows Forcipol and Forcimat that were used to smoothen the surface of the thin section. This process takes a long time as the surface need to be very smooth with thin layer which requires a slow process so that the rock sample will not crack.

The same procedures are also taken to prepare the core plug samples for the SimpangPulai carbonate rocks.

3.1.2 Experiment set up

A. Acid dissolution

Apparatus: caliper, thermometer, pH electrode, beakers

Chemicals: 0.01M hydrochloric acid and 0.01M acetic acid

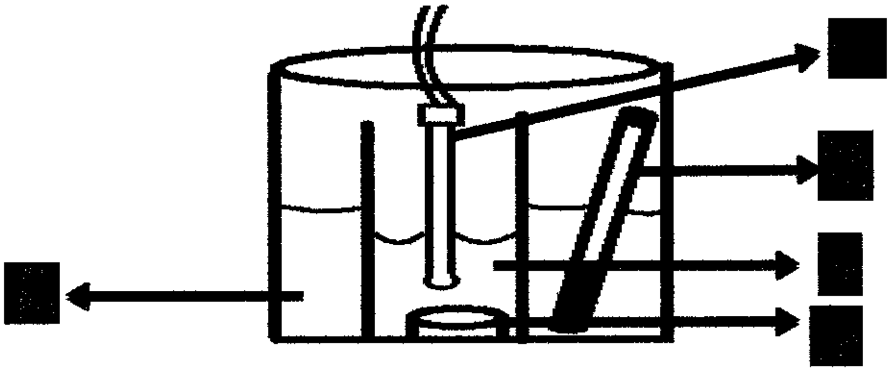


Figure 1.13 shows the experimental set up with:

A = pH electrode, B= Thermometer, C=Acid solution 0.01M, D=Core plug sample, E= constant temperature water bath at atmospheric temperature of 25^{0}C.

Procedures:

1. Firstly the effective diameter and thickness of each core plug samples are measured using the calliper.
2. The experiment set up is as shown in the Figure 1.13. It consists of a beaker that contains 500 mL of acid solution of 0.01M which is held in a constant temperature bath at room condition of 25^{0}C and pressure of 1 atm.
3. The pH reading of the acid solution inside the beaker is taken using the pH electrode. The core plug sample is placed inside the beaker and the reaction time starts. The pH reading is taken every hour for the first five hours of reaction and subsequently one a day for the next two weeks.
4. The acid solution inside the beaker is changed once the pH reading of the acid solution increased to 5.5. The leftover acid solution reacted with the core plug sample is then used for Calcium content analysis in the lab.
5. All runs of the core plug samples were made in duplicates.

6. The porosity and permeability analysis of the core plug samples were done before and after the acid dissolution was conducted in order to compare the changes that may occur.
7. For core plug samples is then tested for it strength.

B. FTIR

FTIR- Fourier Transform Infra-red or infrared spectroscopy uses infra-red radiation to pass through a sample which will absorb some of it and the rest is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission or known as molecular fingerprint of the sample. Thus, it can be used to find:

- Identify unknown materials
- Determine quality or consistency of a sample
- Determine the amount of components in a mixture

The instrumental processes are as below: [21]

1. **The source**: Infrared energy is emitted from a glowing black-body source. The beam passes through an aperture which controls the amount of energy presented to the sample.
2. **The Interferometer**: The beam enters the interferometer where the "spectral encoding" takes place. The resulting interferogram signal then exits the interferometer.
3. **The Sample**: The beam enters the sample compartment where it is transmitted through or reflected off the surface of the sample, depending on the type of analysis being accomplished. The specific frequencies of energy which is uniquely characteristic of the sample are absorbed.
4. **The Detector**: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.
5. **The computer**: The measured signal is digitalised and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

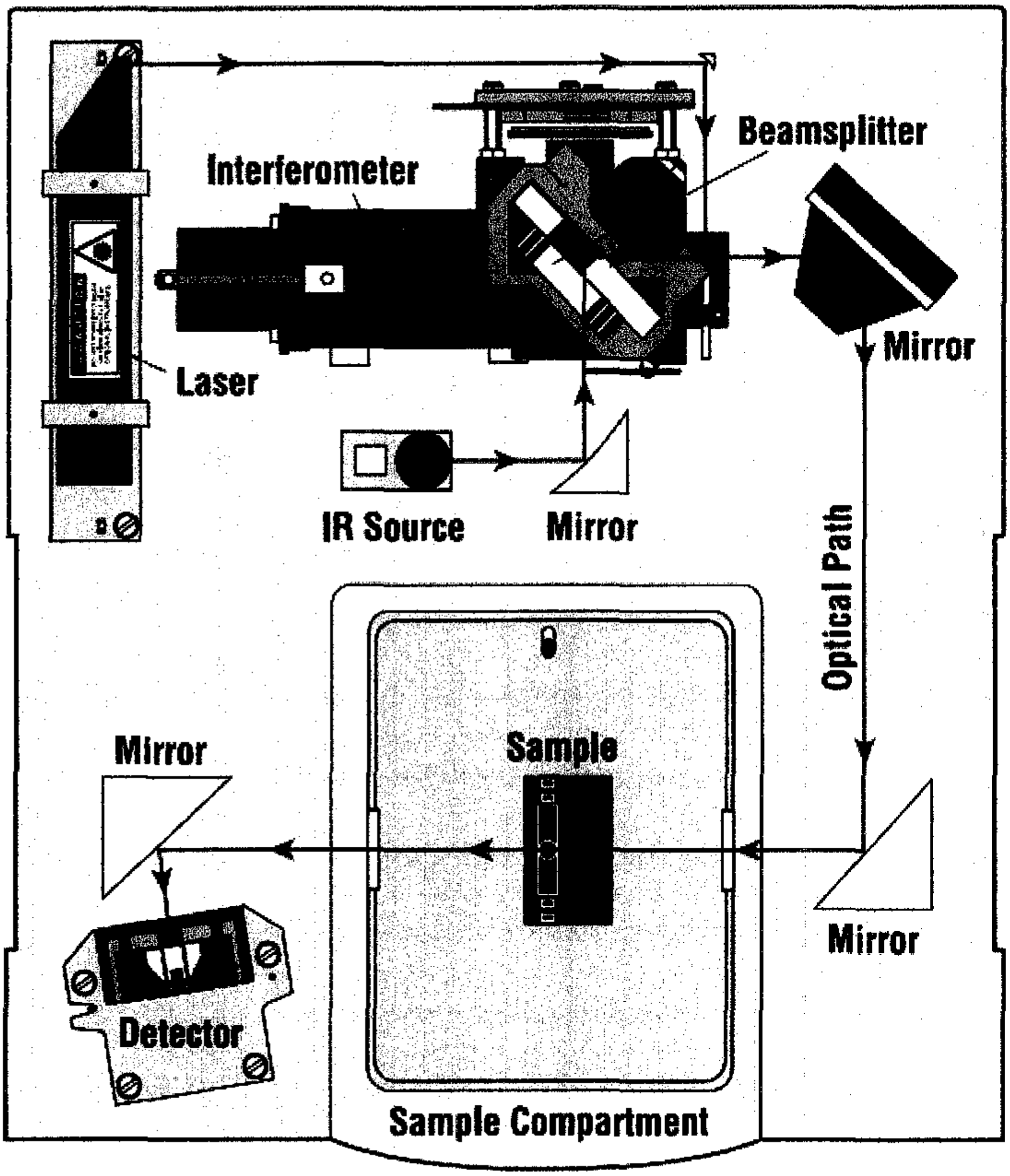


Figure 1.15 shows the simple layout of a spectrometer. [21]

3.4 Key Milestone

No	Action Item	Action By	Date	Note
1	Briefing & update on students progress	Coordinator / Students / Supervisors	8 FEB	WEEK 3
2	Project work commences	Students		WEEK 1 - 14
3.	Submission of Progress Report	Students	16 MARCH	WEEK 8
4.	PRE-EDX combined with seminar/ Poster Exhibition/ Submission of Final Report (CD Softcopy &Softbound)	Students / Supervisor / Internal Examiner / Coordinator	4 APRIL	WEEK 11
5.	EDX	Supervisors / FYP Committee	11 APRIL	WEEK 12
6.	Final Oral Presentation	Students / Supervisors	20 APRIL 2011	WEEK 13
7.	Delivery of Final Report to External Examiner / Marking by External Examiner	FYP Committee / Coordinator	20-27 APRIL 2011	WEEK 14
8.	Submission of hardbound copies	Students	04 MAY 2011	WEEK 16

Table 1.2 shows the list of all key milestones

3.5 Gantt Chart

Item/ week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Literature review	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
Progress report								🟥						
Experiment	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪				
SWOT analysis								🟧						
Dissertation								🟩	🟩	🟩	🟩	🟩	🟩	🟩
Pre-EDX											🟦			
Oral Presentation														🟥

Table 1.3 shows the Gantt chart of the project

3.6 Tools

- Metkon (COREX S25 1-fas, FORCIMAT-TS, MICRACUT 175 and GEOCUT)
- Bruker-AXS, D8 Advance X-Ray Diffraction (XRD)
- Bruker-AXS, S4 Pioneer X-Ray florescence (XRF)
- Shimadzu machines for (AS-3000 SEM, AA-6800 AAS, and AF-6400 FTIR)
- Vinci Technologies, Coval 30 Poro-perm
- O-I-Analytical 1020A (TOC)

4 Results and Discussions

4.1 Experimentation

From this experiment, we should be able to see a difference in kinetic dissolution rate of the carbonate sample rock taken from Sungai Siput and from SimpangPulai. This is because the grains of the samples have undergone different level of changes due to different level of exposure to geothermal effects. Moreover, the chemical composition of the samples should be different since different chemical components have different rate of dissolution. The strength of the carbonate rock which has undergone acid dissolution should also be changed. The weaken strength maybe be able to explain the collapse of cave which has been exposed to erosion. Thus such structure will be unsafe for any activities.

A porosity and permeability analysis will enable us to see how these changes occur as a result of the acid dissolution. These data are important especially in estimating the effectiveness of increasing permeability of carbonate rock. The data collected will be used to simulate how acid stimulation jobs in carbonate reservoir are suitable to be conducted in these rock samples. The time needed and the effect of both organic and mineral acid will also be compared to see the effectiveness of the type of acid used

An SEM analysis of the structure of the rock samples will give a picture of how the pore architecture of the sample looks like before and after it has been dissolved by the acid.

The thermal conductivity of the sample should also differ.

4.2 Data Gathering and Analysis

4.2.1 XRF

Sample	Percentage of elements (%)		
	O	Ca	Sr
Sungai Siput limestone	29	71.35	0.148
SimpangPulai limestone (fine white grain)	29	71.47	-
SimpangPulai limestone (coarse white grain)	29	71.47	-
SimpangPulai limestone (darker grain)	29	71.47	-

Table 1.4above shows the XRF percentage of elements analysis.

From the data above, all three samples of SimpangPulai limestone has similar content of Oxygen and Calcium. Meanwhile, the Sungai Siput sample indicated low amount of Strontium (0.148%) presence.

4.2.2 Thermal Conductivity

A= r^2 , d= 1.5 inches=3.81cm=0.0381m

$\therefore A = \pi(\frac{d}{2})^2$= 1.14 e-3 m^2

Q=100 watts

Fourier's Law of heat conduction

$$q = \frac{KA\Delta T}{L} = \frac{Q}{3600}$$

$$K = \frac{(Q/3600)L}{A\Delta T}$$

Sample	T1 (^{0}C)	T2(^{0}C)	ΔT(^{0}C)	L (cm)	K (W/m ^{0}C)
S.S LS 1	30.1	29	1.1	1.6	0.3544
S.S LS 2	33.1	29.2	3.9	1.8	0.1125
S.P LS D	36.9	31.1	5.8	2.6	0.1092
S.P LS C	27.1	21.9	5.2	2.6	0.1218
S.P LS F	40.1	35.6	4.5	2.5	0.1354

Table 1.5 above shows the thermal conductivity of the sample rocks

S.S LS – Sungai Siput Limestone
S.P LS D- SimpangPulai Limestone (dark grain)
S.P LS C- SimpangPulai Limestone (Coarse grain)
S.P LS F- SimpangPulai Limestone (fine grain)

From the table above, we can see a difference in value of the thermal conductivity of the Sungai Siput Limestone due to the different orientation used during the experiment.

Overall for the SimpangPulai limestone, the white grain limestone has higher thermal conductivity compared to the darker grain one. Moreover, the fine grain sample has higher thermal conductivity value than the coarser grain as it has a larger surface area to transmit heat.

4.2.3 SEM

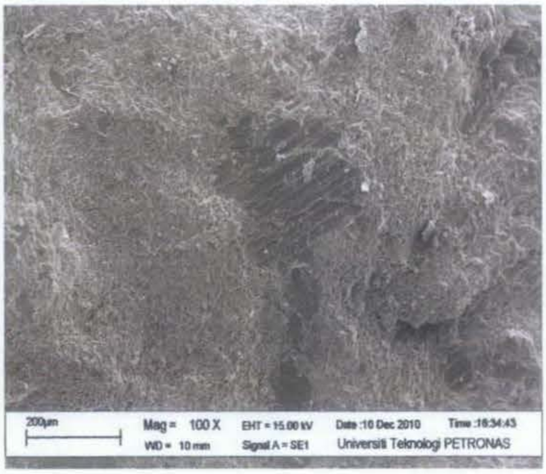


Figure 1.16

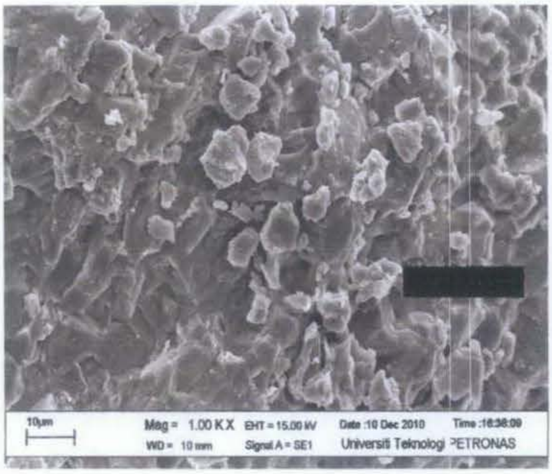


Figure 1.17

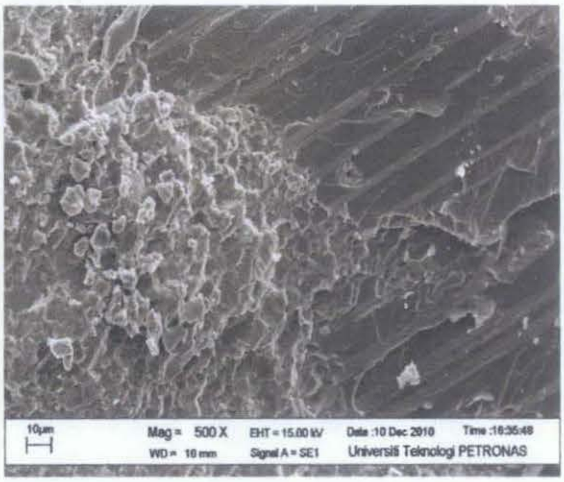


Figure 1.18

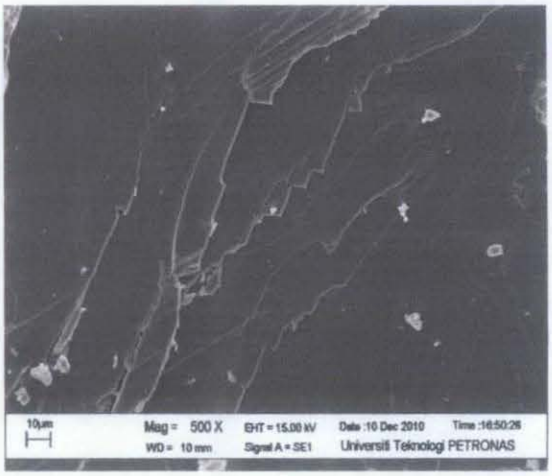


Figure 1.19

Figure 1.16-1.19 shows the SEM for Sungai Siput limestone at magnifications of 100X, 500X, 100X and 500X respectively. There are two different calcite matrix in figure 1.16. This is clearly shown when the image is taken closer at the contact area of the two distinct matrixes in figure 1.18. A closer picture of the spheritic matrix is shown in Figure 1.17 and a closer picture of the lamella of the other matrix is shown in figure 1.19.

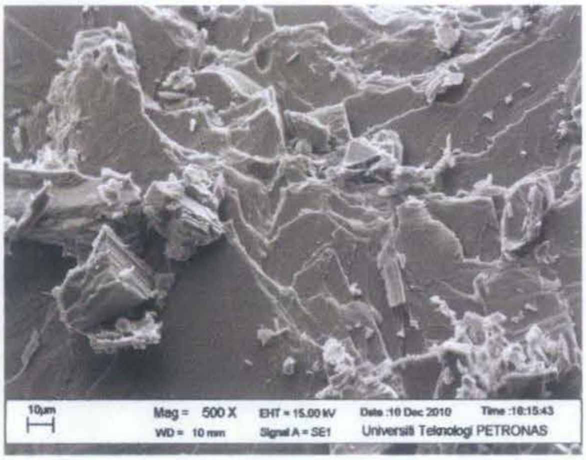


Figure 1.20

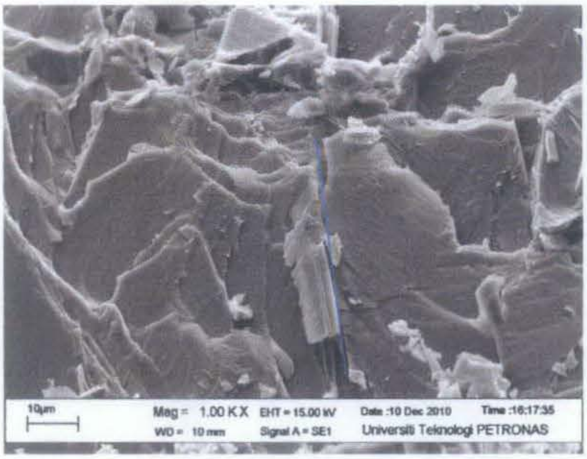


Figure 1.21

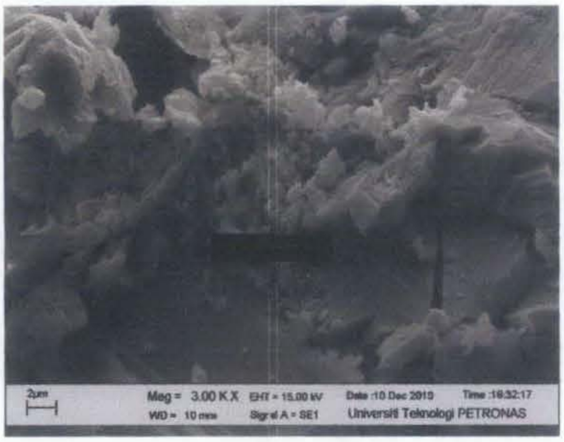


Figure 1.22

Figure 1.20-1.22 shows the white fine grain SimpangPulai limestone SEM photos at 500X, 1000X and 3000X magnification respectively. It shows that there is fracture line in figure 1.21 as indicated by the blue line. Meanwhile Figure 1.22 shows the smallest size of a molecule at 558.3 nm.

Figure 1.23

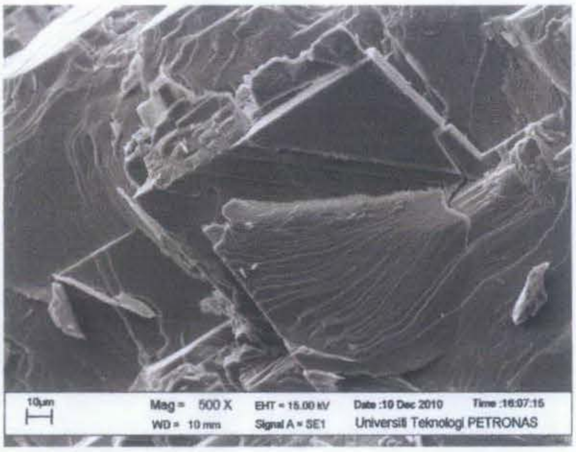


Figure 1.24

Figure 1.25

Figure 1.23 and 1.24 shows the SEM photos for white coarse grain SimpangPulai Limestone at 500X magnification. It shows the cleavages of the matix in figure 1.24.

Figure 1.25 shows the SEM photo of the dark grain SimpangPulai Limestone at 500X magnification. It shows the lamellae of the matrix.

4.2.4 XRD

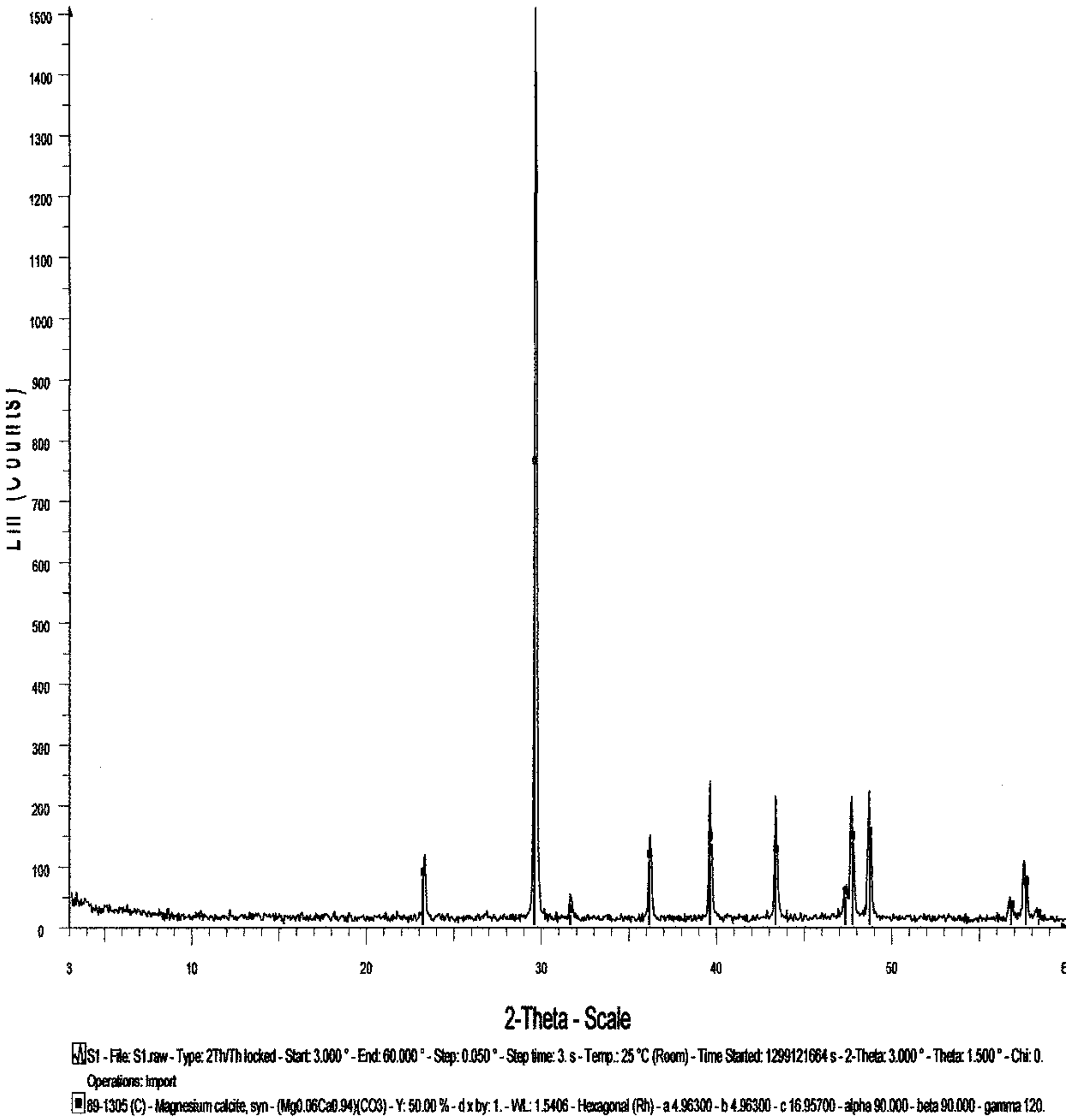


Figure 1.26 shows that Sungai Siput limestone has high content of Calcite of 94% and low content of dolomite of 6%

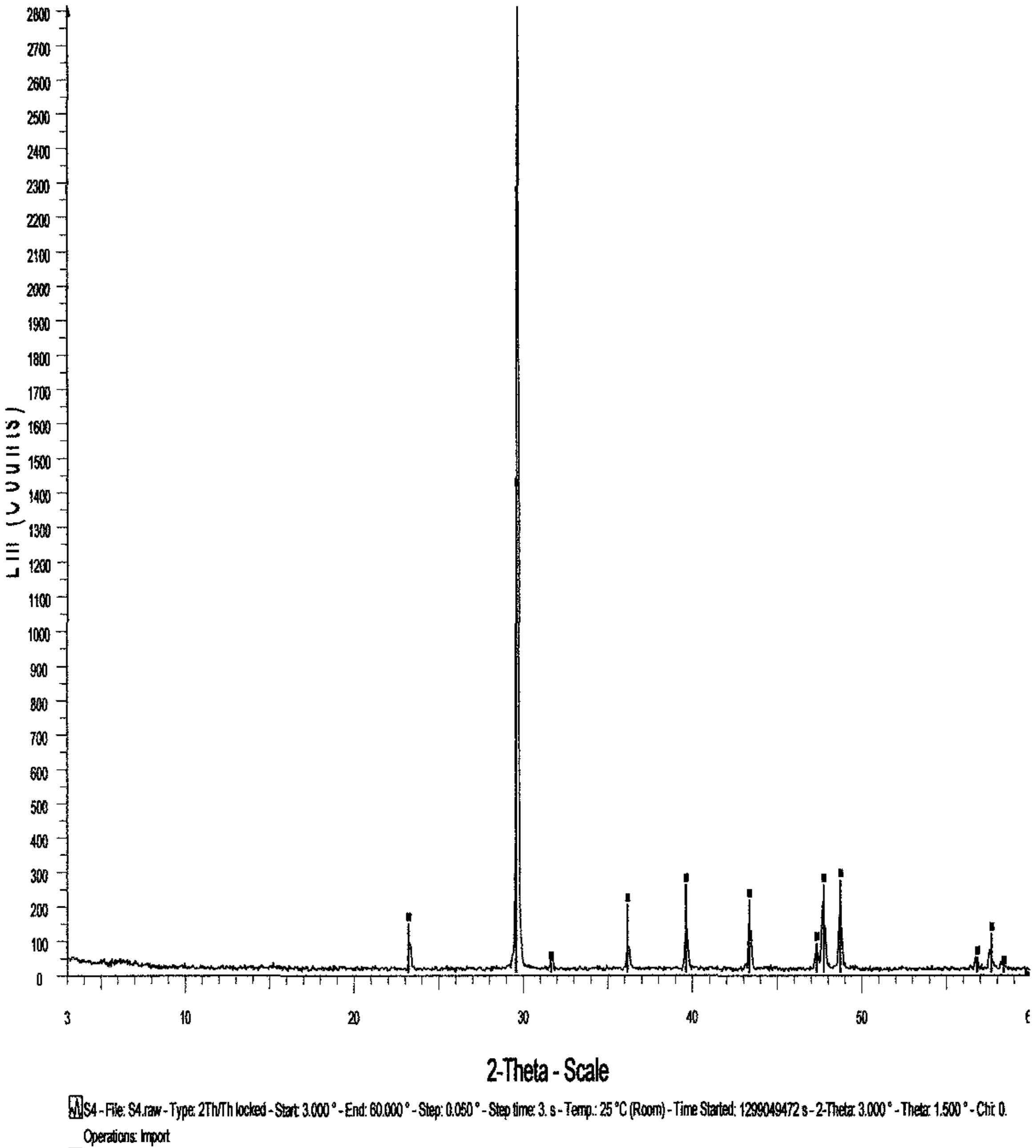


Figure 1.27 shows fine white grain SimpangPulai limestone has high concentration of calcite of 94% and low amount of dolomite of 6%

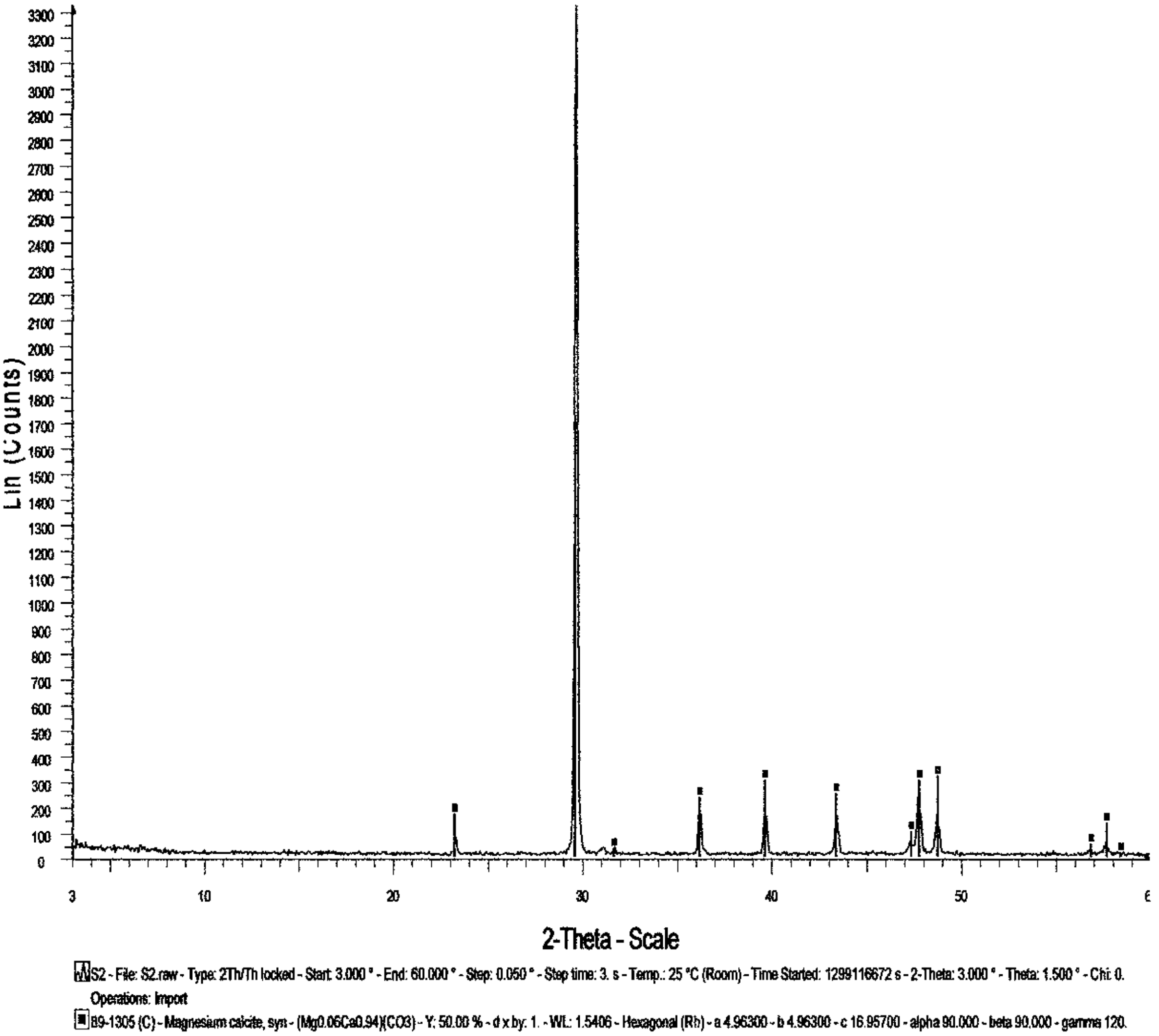


Figure 1.28 shows that coarse white grain SimpangPulai limestone has high concentration of calcite of 94% and lower concentration of dolomite of 6%

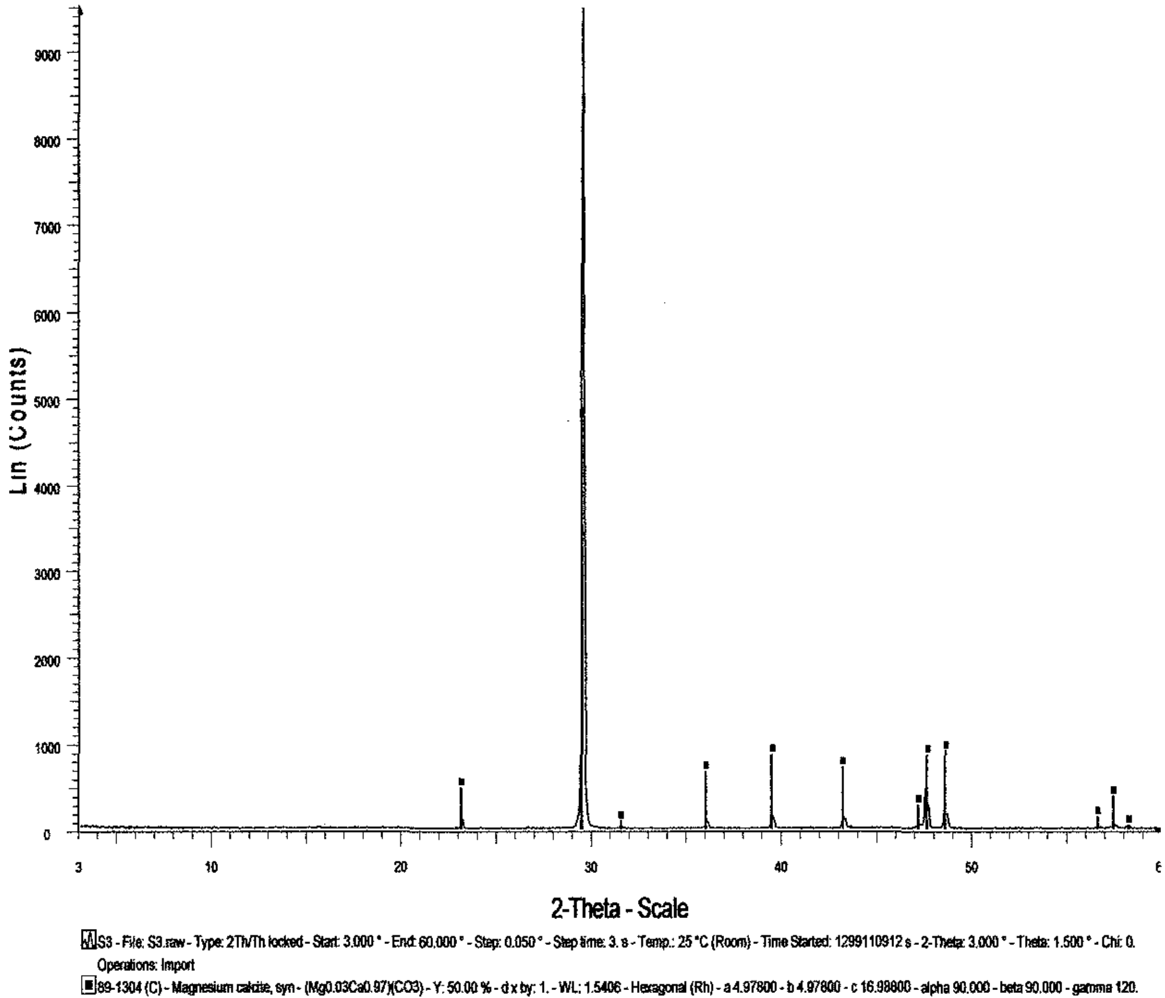


Figure 1.29 shows that darker grain SimpangPulai limestone has higher concentration of calcite of 97% and lower concentration of dolomite of 3%

Discussion:

All the samples have almost similar content of calcite which is high at 94-97 percent and lower amount of dolomite at 3-6%. As such the dissolution is mostly contributed from the dissolution of calcite in the acid. Moreover, the slightly higher concentration of calcite in the darker grain SimpangPulai limestone maybe due to its higher calcite concentration.

4.2.5 TOC

		TOC		
Sample	sample size (mg)	Area (cts)	Mass (mg C)	Conc (% Carbon)
Sungai Siput	186.7	2138	3.31	1.77
Fine white grain SimpangPulai	184.6	1952	3.022	1.64
Coarse white grain SimpangPulai	182.4	1917	2.968	1.63
Darker grain SimpangPulai	183.1	1489	2.305	1.26

Table 1.6 shows the result from the Total Organic Carbon content test. It shows that all the samples have almost similar content of organic carbon which maybe from the phytoplankton and terrestrial plants deposited.

4.2.6 AAS

Difference between the rate of acid dissolution for both acid and the sample type. Overall, hydrochloric acid dissolves more calcium than acetic acid as it a strong acid. Meanwhile, acetitic acid reacts faster than hydrochloric acid as it has a higherpka (acid dissociation constant) of 4.76 versus 2 for the later (as such the pH value increases the fastest for acetic acid). Thus, acetic acid only dissolves partially in the presence of water compared to full dissociation for strong acid like hydrochloric acid.

As such, we can see that the concentration of Calcium in cumulative ppm for those in hydrochloric acid is almost about twice as much as in the acetic acid. The experiment shows that the darker grain SimpangPulai dissolves most followed by the white fine grain SimpangPulai and white coarse grain SimpangPulai and lastly the Sungai Siput limestone

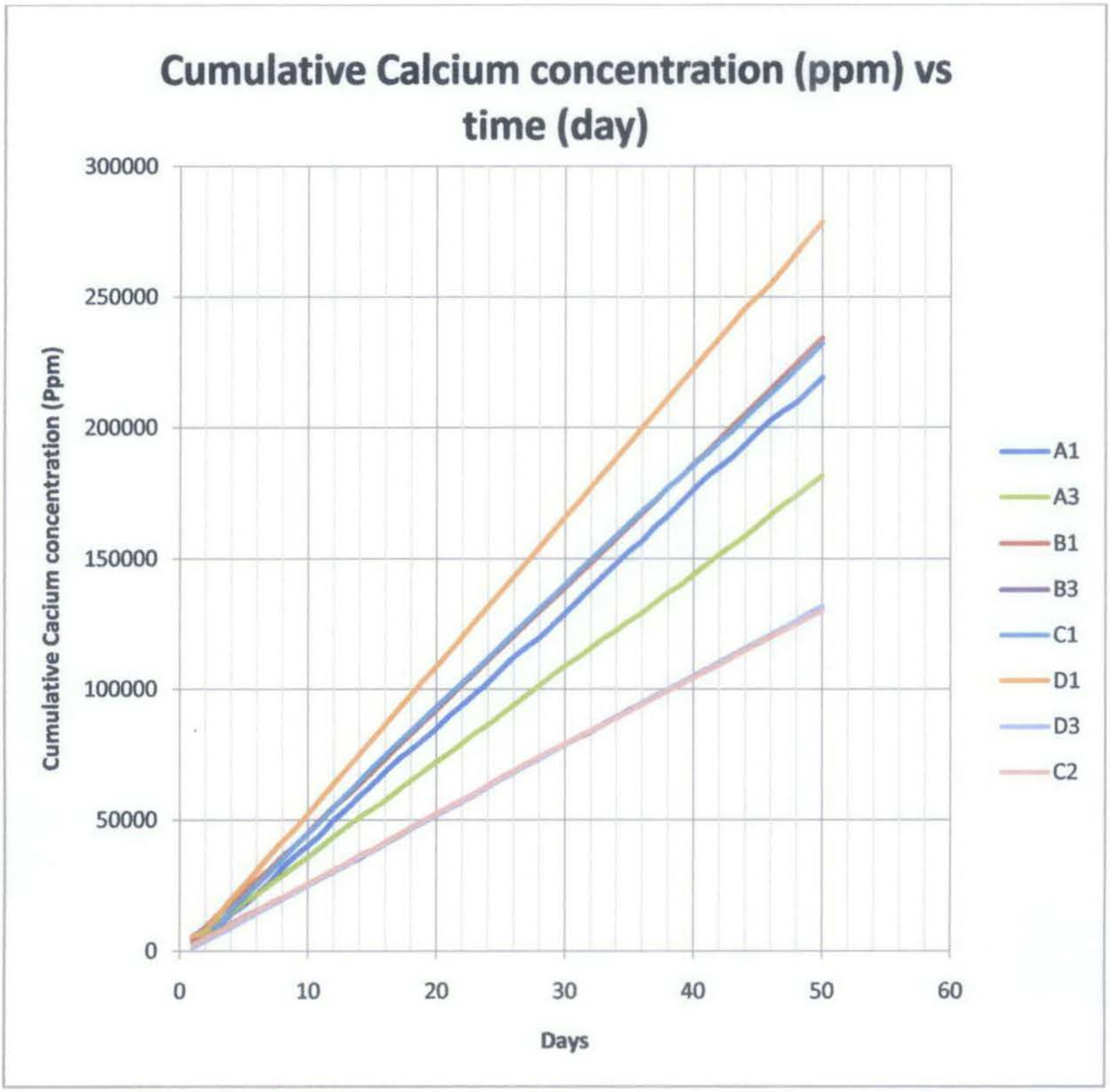


Table 1.7 shows the cumulative Calcium concentration (ppm) vs time of the dissolution. Where A1, B1, C1, and D1 is dissolved in hydrochloric acid and A3, B3, C2 and D3 is dissolved in acetic acid. Sample A is for Sungai Siput limestone, B for white fine grain SimpangPulai, C for white coarse grain SimpangPulai, and D for darker grain SimpangPulai

4.2.7 FTIR

Figures 1.42 to 1.45 in appendices shows the FTIR result for all the samples. Below is the interpretation of the type of bond that exist within the sample using Infrared Functional group for interpretation of FTIR result chart found in the appendices.

Sungai Siput Limestone	711.68	CH2 rocking coverted
	2513.07	COOH Overtone Bands (acid group)
	2873.74	CH3 stretch symmetric
	2981.74	COOH Stretch Antisymmetric (acid dimer)
	3448.49	OH Stretch Broad
Fine White Grain SimpangPulai Limestone	676	Aromatic ring Bend Out of plane ring
	710	CH2 Rocking Concerted
	1107	C-O to C-C stretch Anti symmetrically coupled
	1421	COOH Bend/stretch combination (acid group)
	1639	C=C stretch Cis and Vinyl
	2333	COOH Overtone Bands (acid group)
	2362	COOH Overtone Bands (acid group)
	2515	COOH Overtone Bands (acid group)
	2856	CH2 stretch symmetric
	2921	CH2 stretch antisymmetric
	3465	OH Stretch Broad
White Coarse Grain SimpangPulai Limestone	2513	COOH Overtone Bands (acid group)
	2873	CH3 stretch symmetric
	2981	COOH Stretch Antisymmetric (acid dimer)
Darker Grain SimpangPulai Limestone	2515	COOH Overtone Bands (acid group)
	2871	CH3 stretch symmetric
	2983	COOH Stretch Antisymmetric (acid dimer)
	3288	OH Stretch Broad

Table 1.8 shows the interpretation of the type of bond that exist within the samples. It shows that the fine white grain SimpangPulai Limestone has more types of bonding but the other three samples has almost similar bond exist.

4.2.8 Thin section

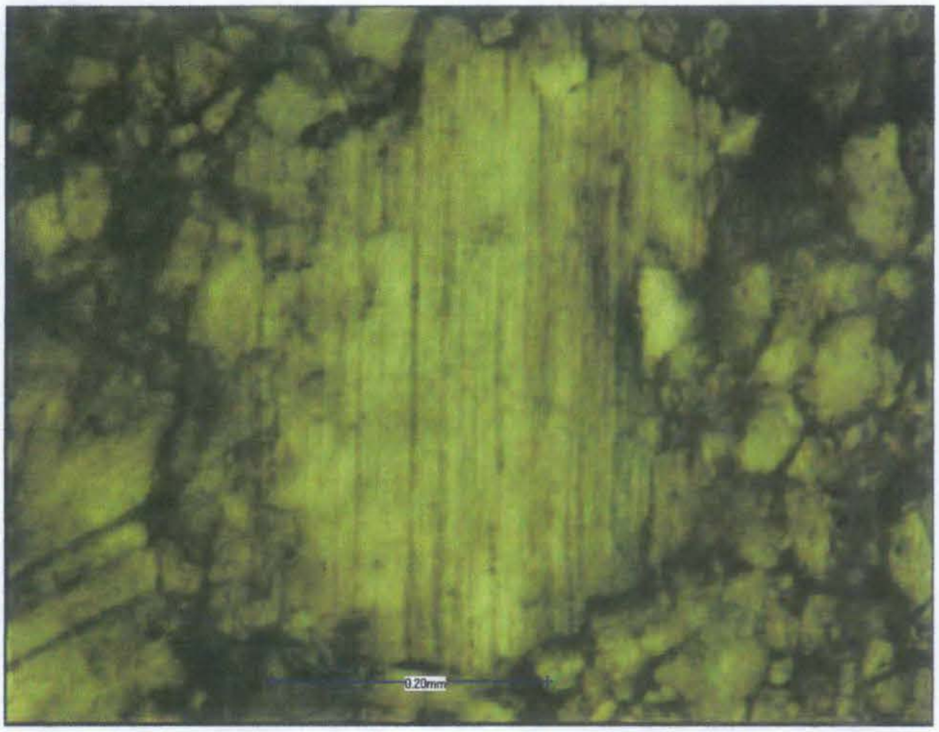


Figure 1.30 above shows the thin section of Sungai Siput limestone. It shows calcite in plane polarized light.

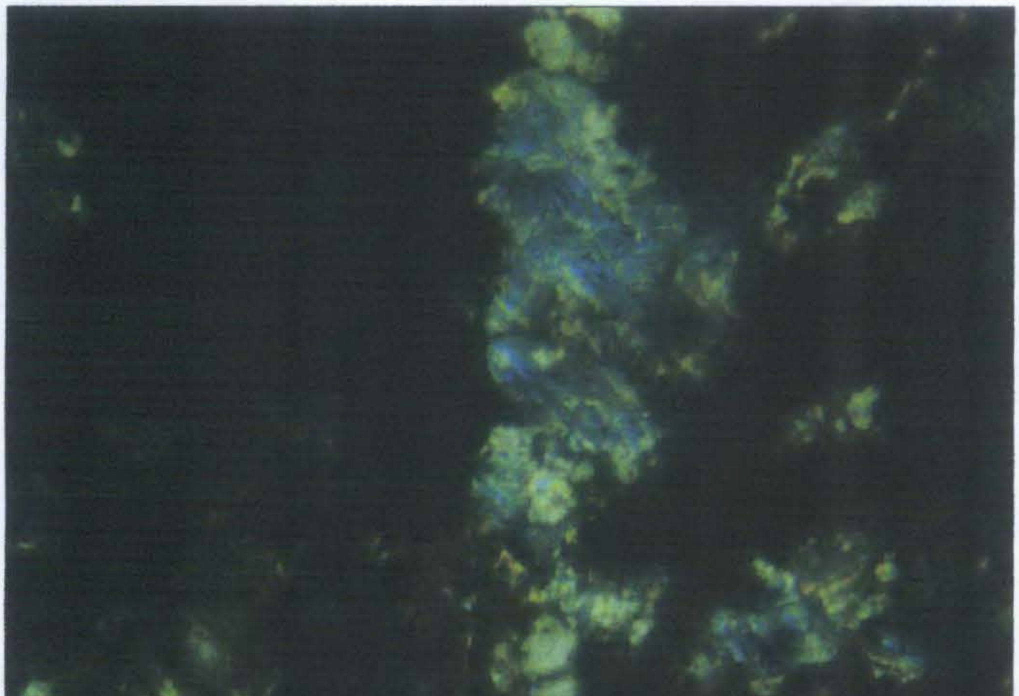


Figure 1.31 above shows the thin section of Sungai Siput limestone. The heterogeneity of the rock samples is reflected in the different optical properties as shown.

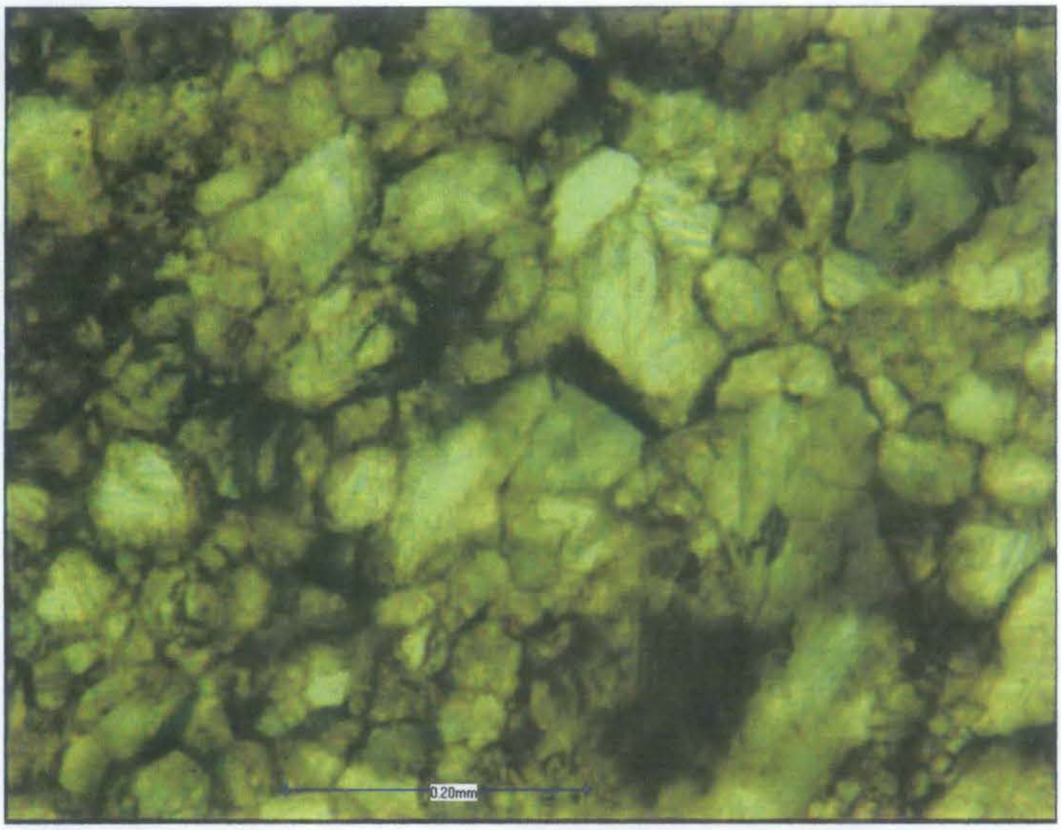


Figure 1.32 above shows the thin section of Sungai Siput limestone. Size of the particles ranges from 50-100 micrometer.

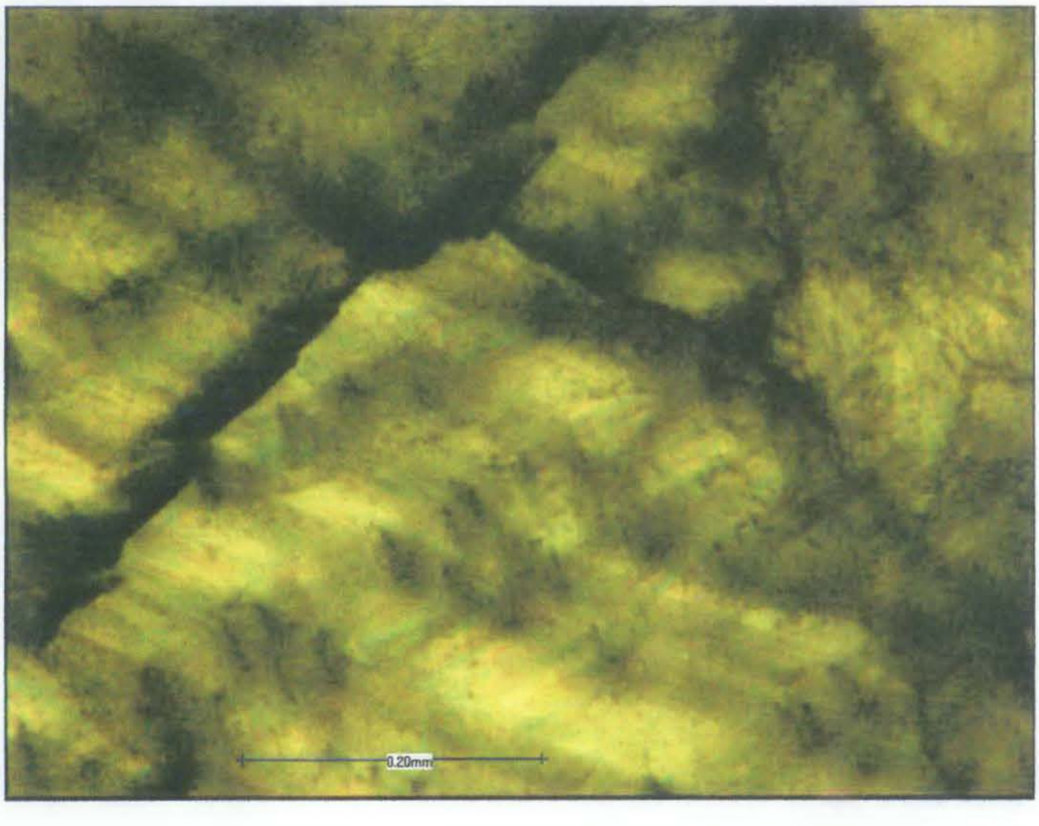


Figure 1.33 shows the thin section of fine white grain SimpangPulai Limestone. It shows the fine calcitic marble

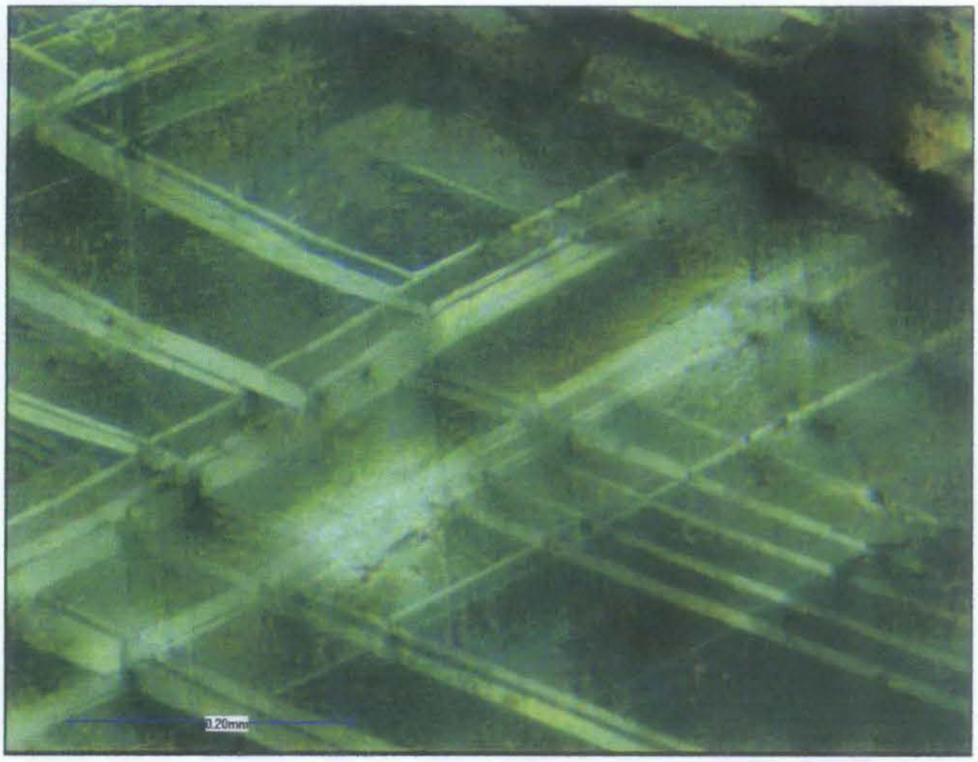


Figure 1.34 shows the thin section of fine white grain SimpangPulai Limestone at 10X magnification with crossed Polaroid lenses. It shows the lamellae in the calcite.

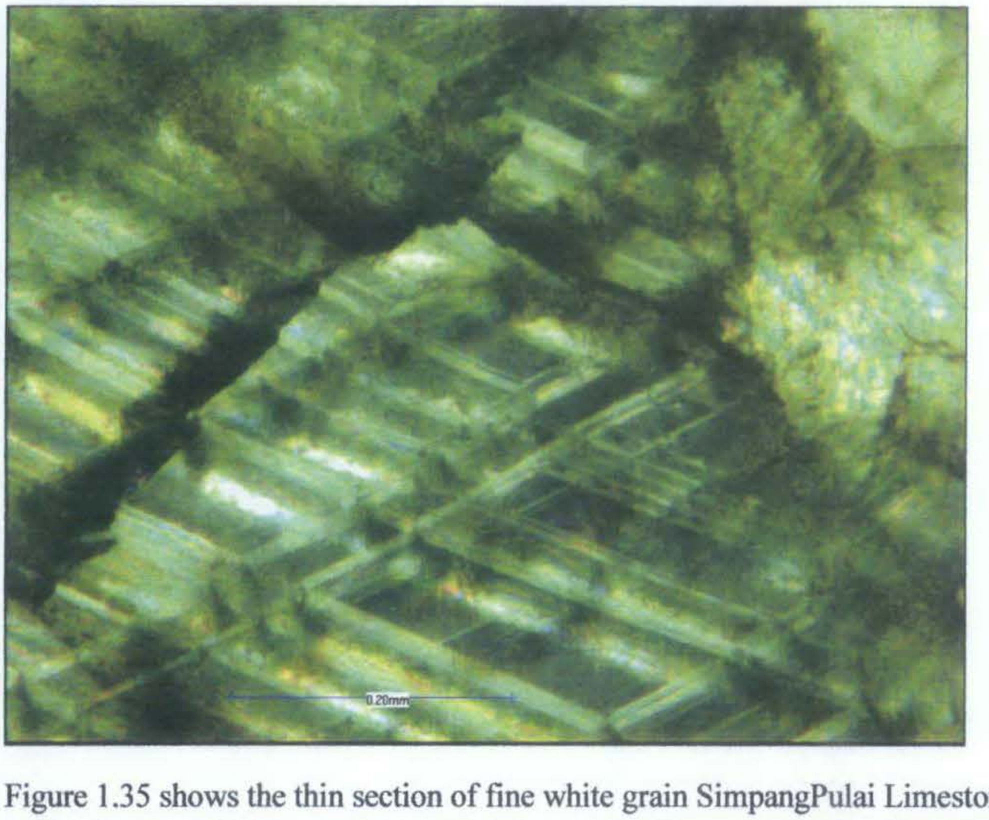


Figure 1.35 shows the thin section of fine white grain SimpangPulai Limestone at 10X magnification with Crossed Polaroid lenses at a different angle of polarisation. It shows lamellae within the calcite.

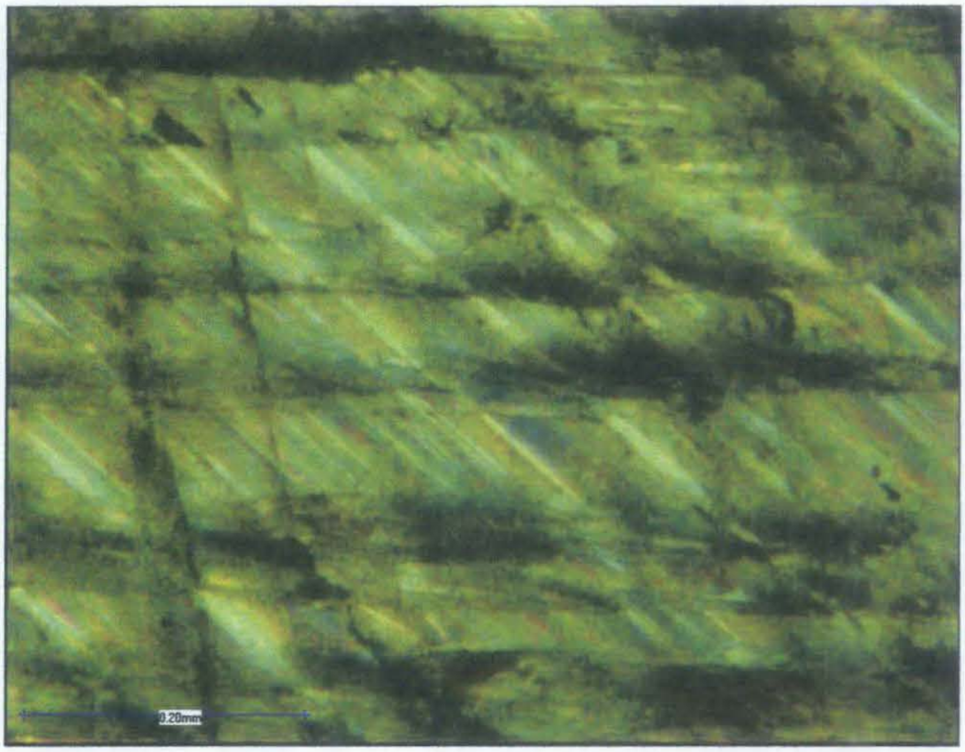


Figure 1.36 shows the thin section of coarse white grain SimpangPulai Limestone at 4X magnification with Polaroid lenses. The angle of the srystal plane is almost 45 degrees.

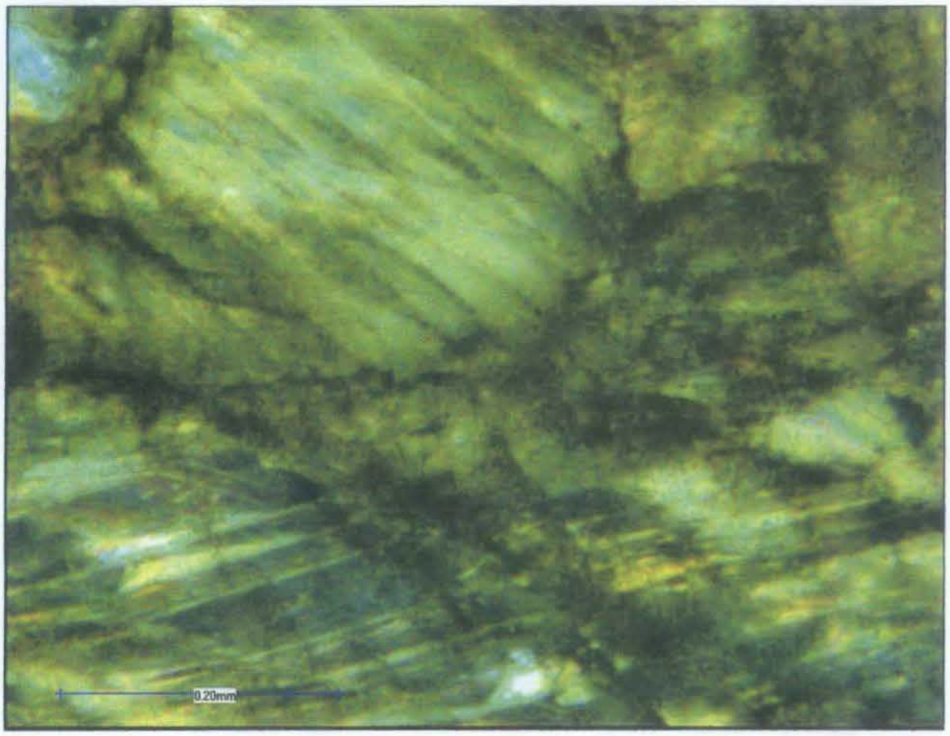


Figure 1.37 shows the thin section of coarse white grain SimpangPulai Limestone at 4X magnification with Polaroid lenses. It shows the crystal plane of a few different matrixes.

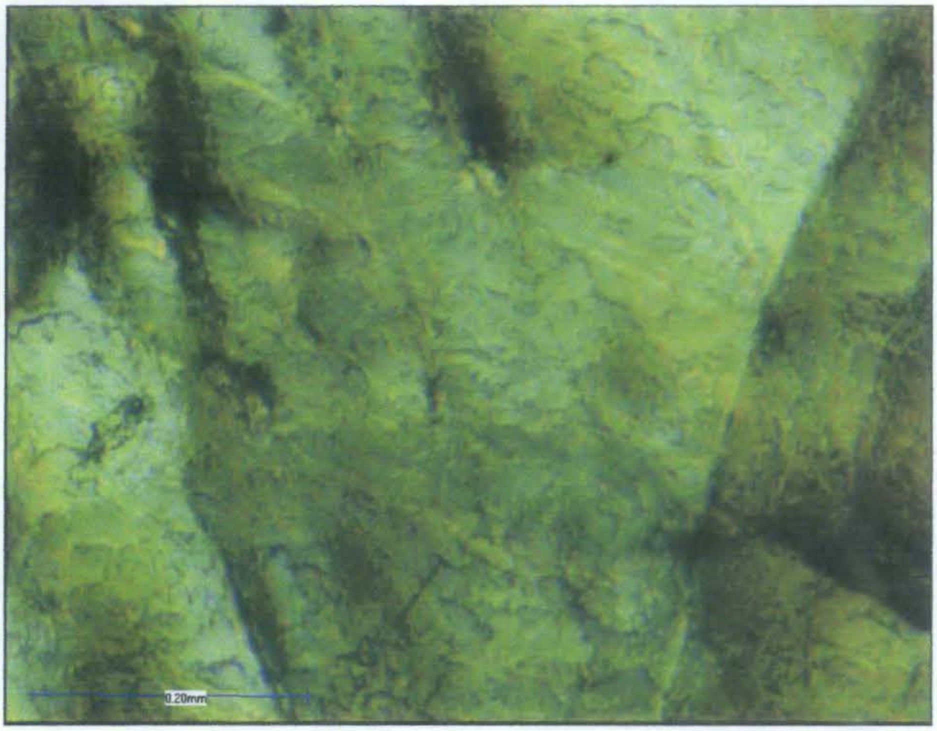


Figure 1.38 shows the thin section of coarse white grain SimpangPulai Limestone at 10X magnification with Polaroid lenses. It shows the fabric of the crystal structure.

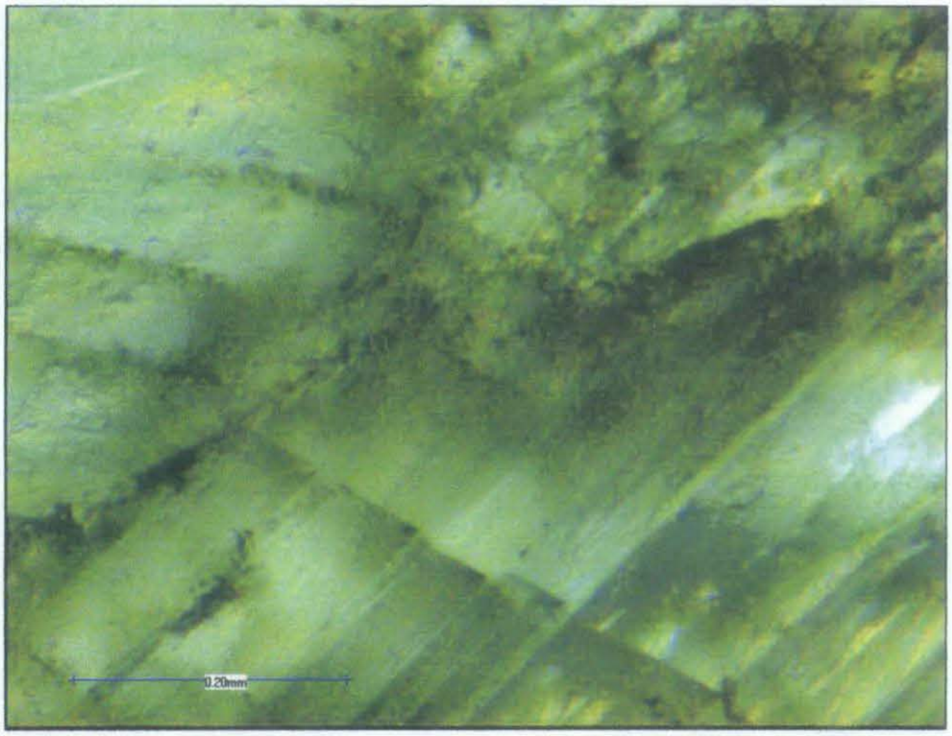


Figure 1.39 shows the thin section of coarse white grain SimpangPulai Limestone at 10X magnification with crossed Polaroid lenses. It shows adjoining crystals with different crystal orientations. This add to the changes in the thermal conductivity and dissolution rate.

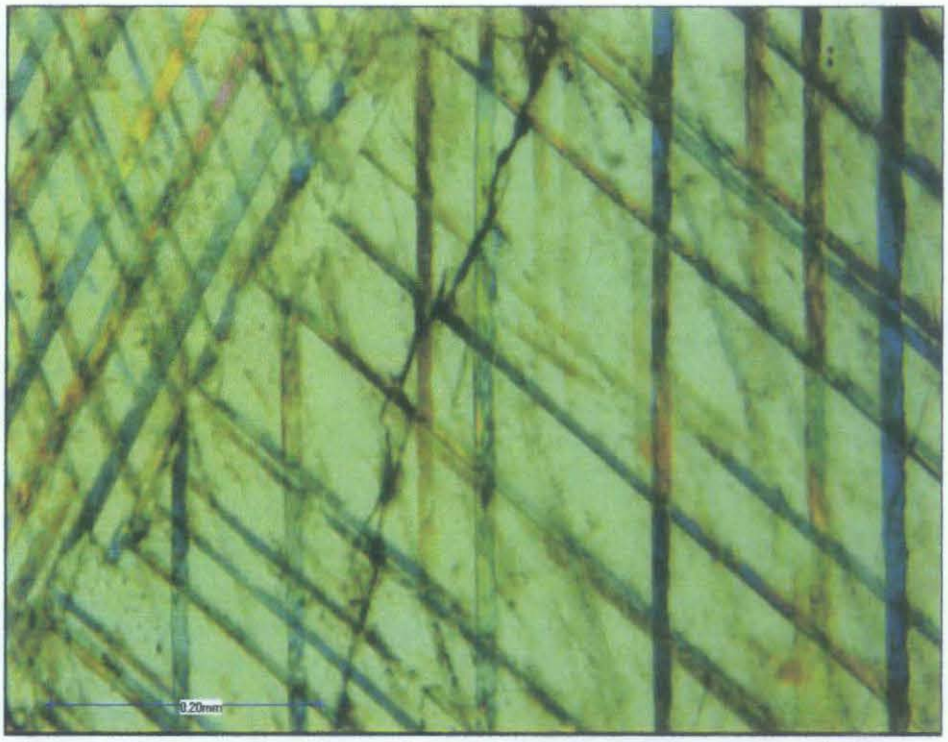


Figure 1.40 shows the thin section of darker grain SimpangPulai Limestone at 4X magnification with crossed Polaroid lenses. It shows iridescence of twin lamellae occurring in both crystal structures.

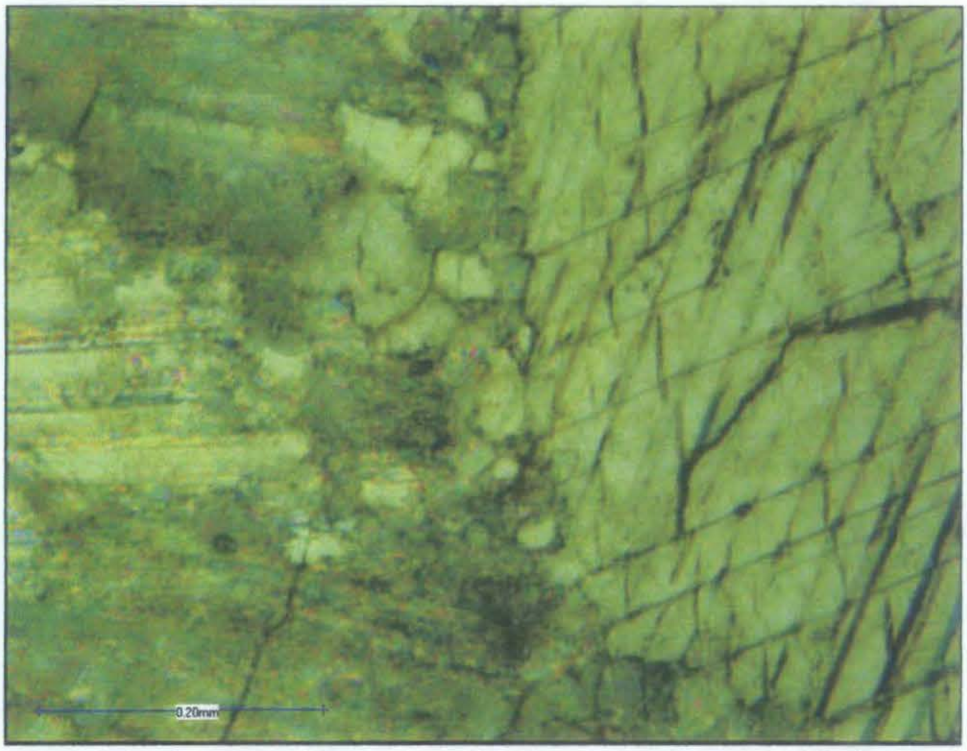


Figure 1.41 shows the thin section of darker grain SimpangPulai Limestone at 4X magnification with crossed Polaroid lenses. It shows the contact of a few rock grains.

5 Conclusion and Recommendation

5.1 Conclusion

Summary

This project is important to analyse the carbonate rock formation that forms in the peninsular Malay mountain belts especially in Perak area. As of now the area along the Malacca Straits has not been explore for its hydrocarbon potential as it is the most important shipping line in the world for the export and import for both Eastern and Western world. However, if there is any economical hydrocarbon potential, a better understanding of the carbonate rock formation in these areas will play an important role as it has great potential in finding carbonate rock as its reservoir.

There are various factors that affect the kinetic of dissolution of carbonate rock. The factors for this project are listed as below:

- All the sample have a different kinetic dissolution rate due to type of ion complexationpresent (as shown in the XRF and XRD results
- The different surface fabric and size as shown in the SEM and thin section photos taken
- The type of bonding that exists between the molecules of the limestone as indicated in the FTIR result.

Conclusion

As the samples were dissolved using low concentration acid within a short time span, there is no significant change in the permeability of the samples observed.

1. From the AAS plot, we can conclude that all the carbonate rock samples have a different dissolution rate as such it different kinetics of dissolution.
2. The change in permeability of the carbonate rocks are too small during this short term study in order for a proper evaluation.

5.2 Recommendations

Suggestion is to have more samples of carbonate rocks taken so that a more comprehensive study of carbonate rock of Peninsular Malaysia can be done. It is suggested that the acid dissolution experiment to be conducted at reservoir temperature and pressure so that if the data gathered can be more representative of the reservoir condition for acid stimulation works effectiveness. Besides a longer period of experiment to be conductor to study how the porewall stability of the carbonate rock changes over the time.

Reference

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Appendices

1. Advantages of FTIR: [21]

- Speed: All the frequencies are measured simultaneously within seconds rather than several minutes by the FTIR. This is also known as Felgett Advantage.
- Sensitivity: Improved FTIR sensitivity is due to several reasons. The detectors employed are much more sensitive, the optical throughput is much higher (Jacquinot Advantage) which results in much lower noise levels and the fast scans enable the co-addition of several scans to reduce the ransom measurement noise to any desired level (signal averaging)
- Mechanical simplicity: The moving mirror in the interferometer is the only moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.
- Internally Calibrated: The instruments employ a HeNe laser as an internal wavelength calibration standard (Connes Advantage). The instruments are self-calibrating.

2. Infrared Functional group for interpretation of FTIR result [22]

Infrared Functional Groups

Group	**Vibration**	Type	**Range**	
CH_3	Stretch	Antisymmetric	2962± 10	
		symmetric	2872± 10	
	Bend	Antisymmetric	1460± 10	
		symmetric	1375± 10	Umbrella
CH_2	Stretch	Antisymmetric	2926± 10	
		symmetric	2853± 10	
	Bend	Scissors	1455± 10	
	Rocking	Concerted	720± 10	Four or more
$=CH_2$	Stretch	Antisymmetric	3080	
		Symmetric	2997	
	Twist	Out-of-plane	993	Mono or Trans only
	Bend	Out-of-Plane	909	Terminal alkene
			1821	Overtone frequency
C=C	Stretch	Cis and Vinyl	1640+ 20	
		Trans, tri and tetra	1670+ 10	
≡CH	Stretch	Normal	3300± 20	Always very sharp
	Bend	Normal	630	
			1238	Overtone frequency
C≡C	Stretch	Normal	2220± 10	Terminal alkynes
			2225± 10	Internal alkynes
C@N	Stretch	Normal	2250± 10	10 to 20 lower when conjugated
CH_2	Bend	Scissoring	1426	Shifted with @
$C(sp^2)$-H (aromatic)	Stretch	Aromatic or unsaturated	3050± 50	Not assigned to specific vibrational modes
Aromatic Ring	Ring Stretch	Symmetric	1590± 10	Non-symmetrical substitution
			1500± 10	Variable intensity
		Sideways	1450± 10	CH_3 bend overlap
	Bend	Hydrogen	730± 20	Out of Plane
		Out of Plane Ring	690± 20	Mono, meta or 1,3,5 substitution
OH	Stretch	OH stretch	3350± 150	Broad
	Bend	Broad	1400± 100	
	Wag	Band	660	Not a good frequency
C-O to C-C	Stretch	Anti-symmetrically coupled	1°: 1050± 25	
			2°: 1125±	

			25	
			3°: 1150± 50	
NH_2	Stretch	Antisymm	3300± 100	
		Symmetrical	3290	
	Bend	Scissoring	1615±15	1° only
	Wag	Band	797	1° and 2° only
CH=O	Stretch/bend	C-H	2820	Hidden under CH stretches
			2735± 15	Not hidden
	Bend	C-H	1395± 10	
C=O	Stretch	C=O	3420	1727 Overtone Frequency
		C=O	1727	Aldehyde
	Stretch	Conjugated	3400	1715 Overtone Frequency
		Conjugated	1715	Ketone
CH_2	Bend	Scissoring	1407	Shifted with carbonyl
COOH	Wag	Out-of-plane OH	935± 15	Acid Dimer
	Stretch	Antisymmetric	3000± 500	Acid Dimer
	Overtone	Bands	2500± 300	Acid group
	Bend/stretch	Combination	1425± 25	Acid group
	Stretch/bend	Combination	1250± 50	Acid group
O-C(O)-C	Stretch	O-C-C	1245± 15	
			1190±30	Higher esters
		C=O	3484	Overtone ester
			1742	ester
O=C-O-C=O	Stretch	Symmetrically	1830± 10	Anhydride
		Antisymmetric	1755± 15	Anhydride

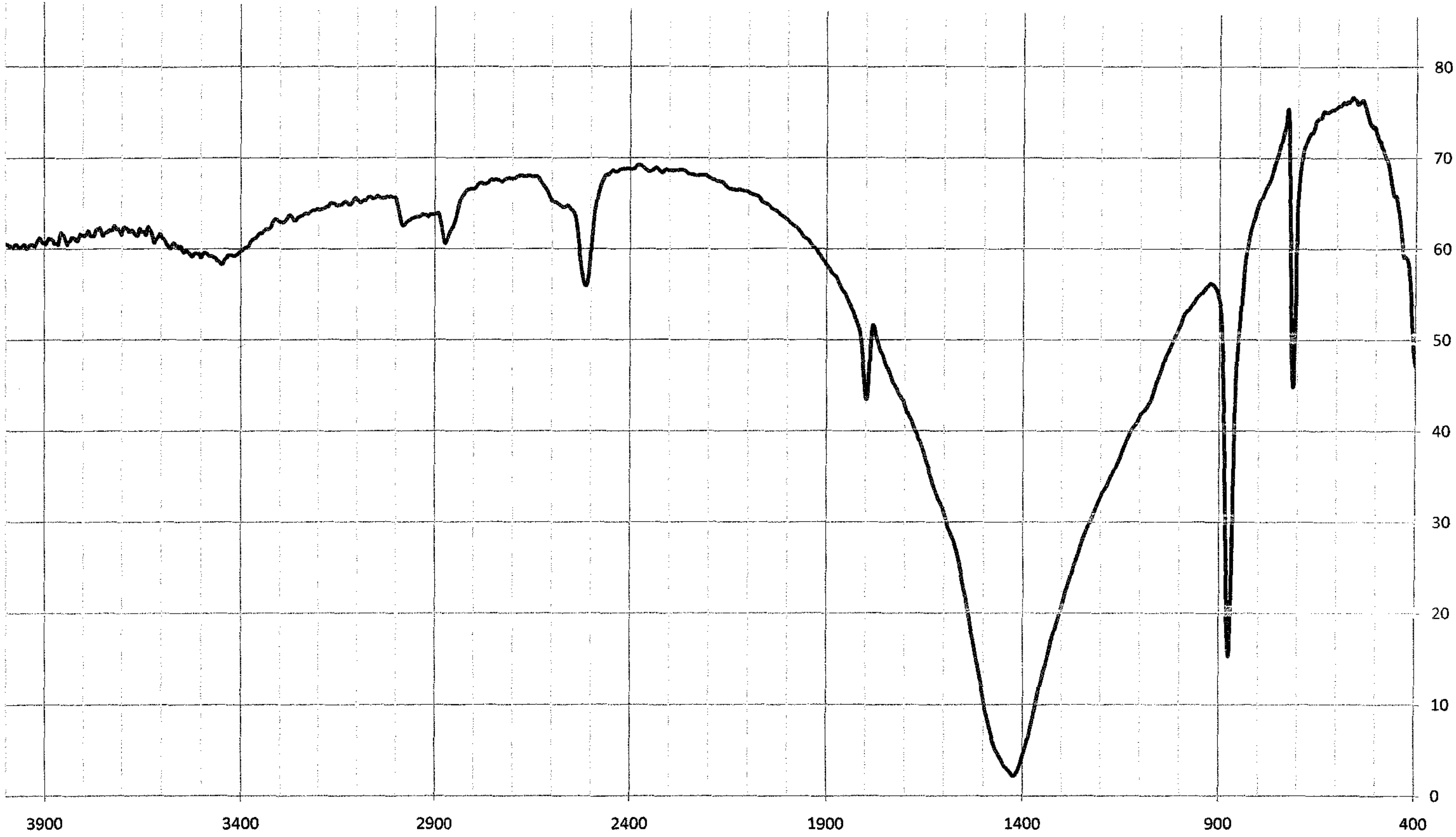

Figure 1.42 shows the FTIR result for the Sungai Siput limestone

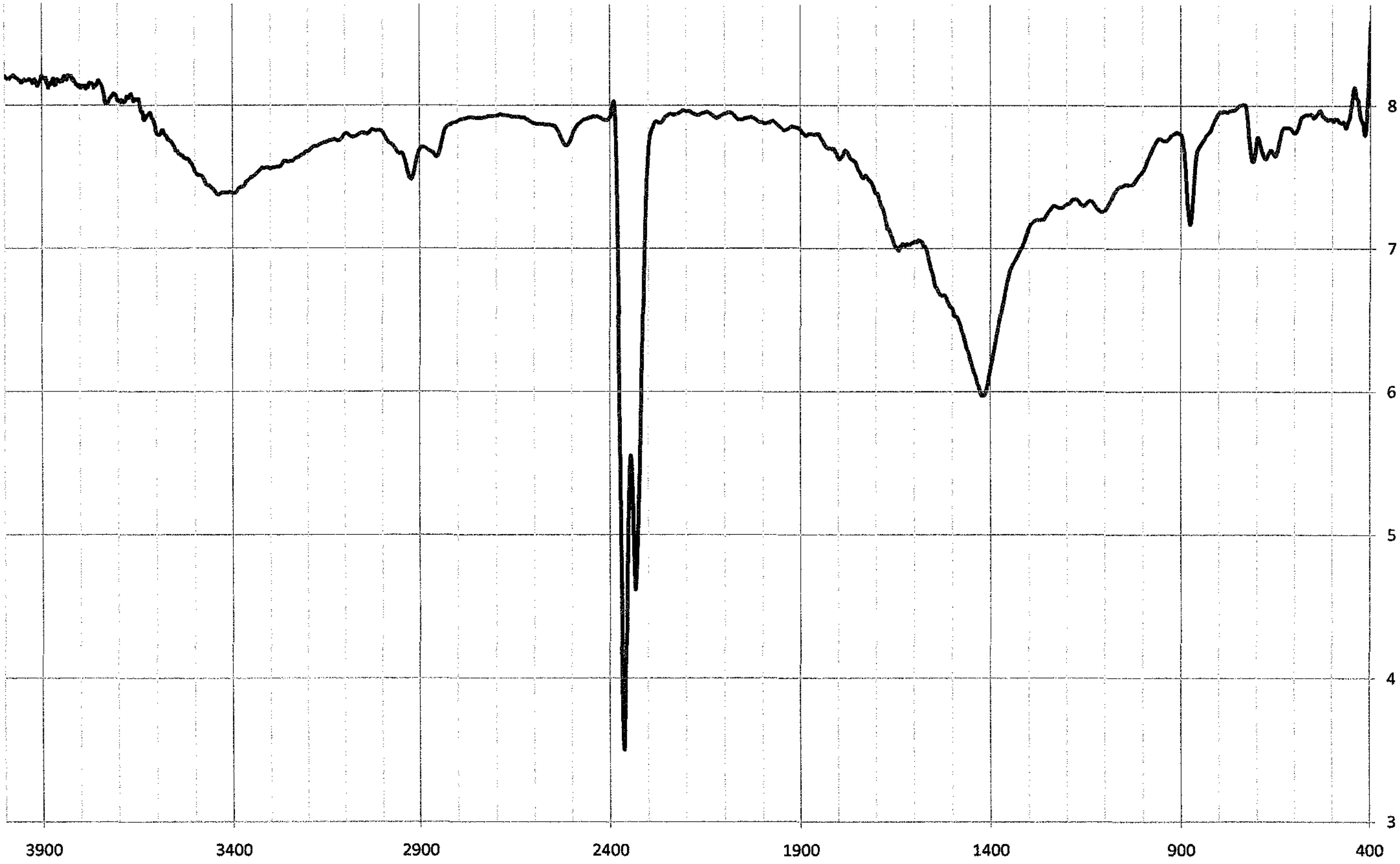

Figure 1.43 shows the FTIR result for the white fine grain Simpang Pulai limestone

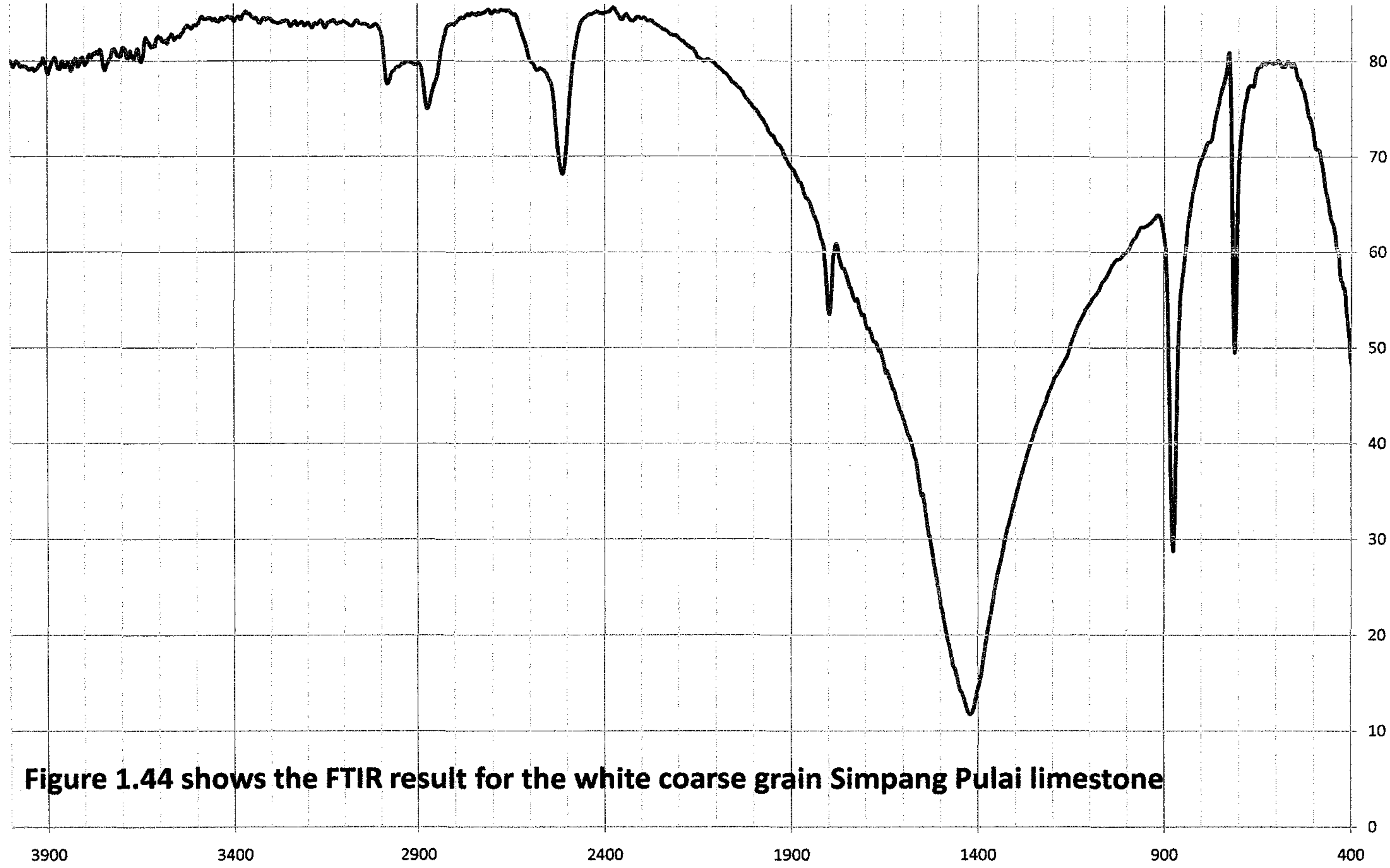

Figure 1.44 shows the FTIR result for the white coarse grain Simpang Pulai limestone

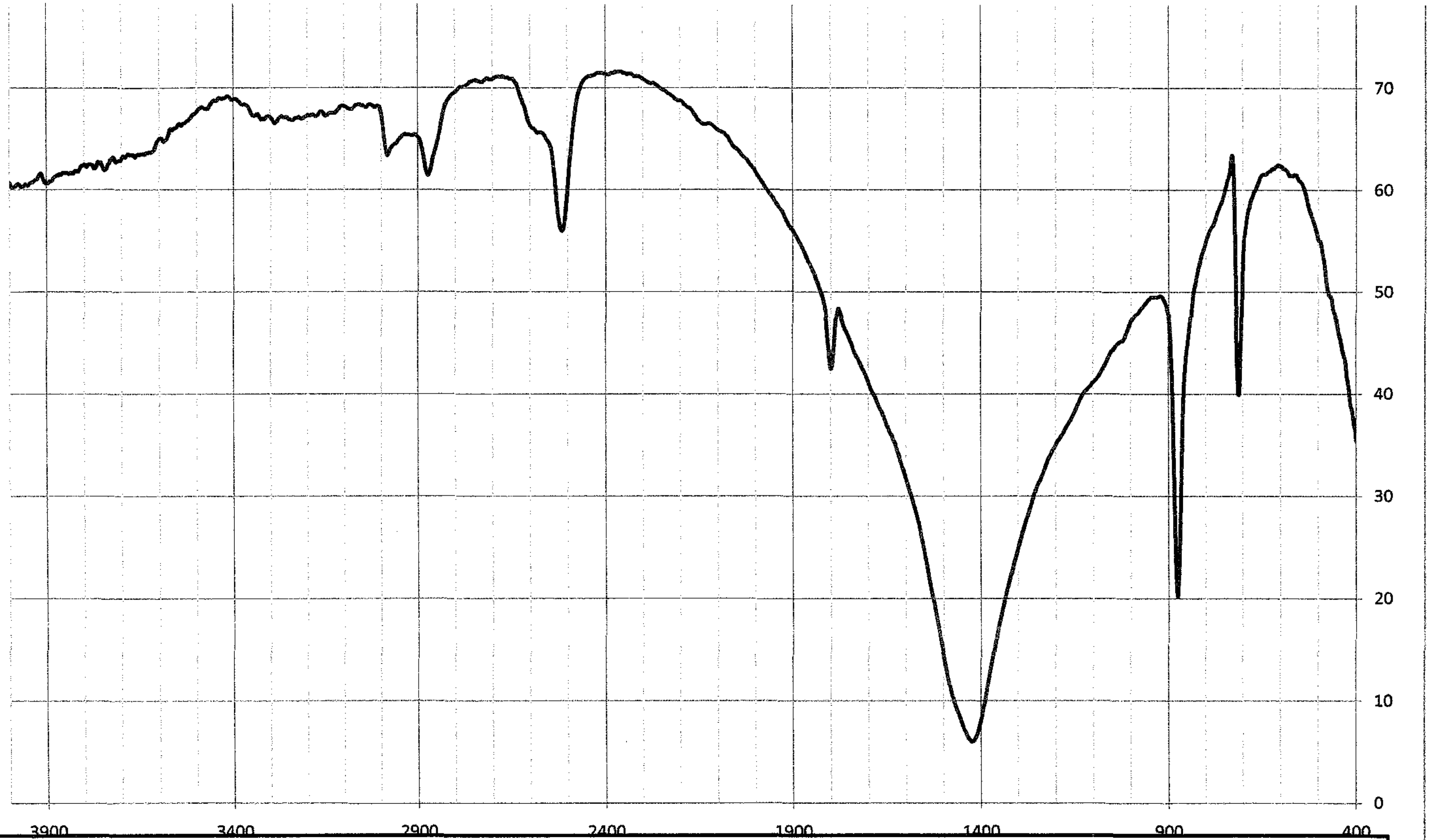

FIGURE 1.45 Shows trhe FTIR results for the Darker grain Simpang Pulai Limestone