## **CERTIFICATION OF APPROVAL**

## Pore-wall Stability in some Carbonates from Sarawak

By

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## **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 sources or persons.

MUHAMAD ZAKWAN B ZAINAL ABIDIN

### ABSTRACT

Carbonates are a class of sedimentary rocks composed primarily of carbonate minerals. The two major types are limestone, which is composed of calcite or aragonite and dolostone, which is composed of the mineral dolomite. There is still a lack of knowledge in the behavior of limestone found in Malaysia to acidification technology. This study is conducted in order to understand the performance of the rock so that we can enhance the production of oil as well as enhance CO2 sequestration. Therefore, the objective of this study is to identify the effects of organic and inorganic acids on the dissolution kinetics of selected carbonates. Pore-wall stability is affected by the fabric of the rock and various geochemical conditions such as mineralogy, composition, solids content, rheology, filtrate and its mineral compositions. External acidizing experiments was conducted in order to understand the behavior and performance of the core samples. From this experiment, the result shows that kinetics dissolution for both samples are higher when immersed in inorganic acid compared to organic acid. This is mainly because inorganic acid have higher value of acid dissociation constant (pKa) compared to organic acid.

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### INTRODUCTION

#### 1.1 Project Background

Carbonates are a class of sedimentary rocks composed primarily of carbonate minerals. The two major types are limestone, which is composed of calcite or aragonite and dolostone, which is composed of the mineral dolomite. [10]

There are two types of carbonate classifications that can be used which is Folk and Dunham classifications. In Folk classifications [1], most limestones are classified as allochemical rocks if they contain over I0% allochems (transported carbonate grains). Based on the percentage of interstitial material, the rocks may be further subdivided into two groups: sparry allochemical limestones (containing a sparry calcite cement of clear coarsely crystalline mosaic calcite crystals) and microcrystalline allochemical limestone (containing microcrystalline calcite mud, micrite, which is subtranslucent gravish or brownish particles less than about 5 microns in size). Further subdivision is based on the allochem ratios of Folk (1962) are shown in Scholle & Ulmer-Scholle (2003). For Dunham classifications, if the grains of a limestone are touching one another and the sediment contains no mud, then the sediment is called a grainstone. If the carbonate is grain supported but contains a small percentage of mud, then it is known as a packstone. If the sediment is mud supported but contains more than 10 percent grains, then it is known as a wackestone, and if it contains less than 10 percent grains and is mud supported, it is known as a mudstone.[12] Base on these classifications, the final results are expected to be different for each sample.

#### 1.2 Problem Statement

Nearly half of the world's reserves of hydrocarbons are found in carbonate formations. [7] These formations are highly soluble in acid, so one of the ways to enhance the well productivity is by using acid simulation. [8] Furthermore, there is still a lack of knowledge in the behavior of limestone found in Malaysia to acidification technology. This study is conducted in order to understand the performance of the rock so that we can enhance the production of oil as well as enhance CO2 sequestration.

### 1.3 Objectives of Study

The objective of this study is to:

 Identify the effects of organic and inorganic acid on the dissolution kinetics of selected carbonates.

### 1.4 Scope of Study

- Literature review on dissolution kinetics of carbonates in acids, and matrix acidizing experiments
- Dissolution kinetics experiments where the samples will be tests in two types of acids which are HCL and Formic Acid.

### LITERATURE REVIEW

#### 2.1 Carbonate Rocks [1]

Carbonates rocks are composed mainly of calcium carbonate, CaCO3. There are three main minerals that form carbonates. They are:

- Dolomite (CaMg(CO3)2), a magnesium rich carbonate produced by diagenesis.
- Calcite (CaCO3), most stable calcium carbonate.
- Aragonite (CaCO3), same chemical composition as calcite but differs in crystal structure.

Two of the most widely used classifications are those of Folk (1959, 1962) and Dunham (1962).Most limestones are classified by Folk allochemical rocks if they contain over I0% allochems (transported carbonate grains). Based on the percentage of interstitial material, the rocks may be further subdivided into two groups: sparry allochemical limestones (containing a sparry calcite cement of clear coarsely crystalline mosaic calcite crystals) and microcrystalline allochemical limestone (containing microcrystalline calcite mud, micrite, which is subtranslucent grayish or brownish particles less than about 5 microns in size). Further subdivision is based on the allochem ratios of Folk (1962) are shown in Scholle & Ulmer-Scholle (2003).

Thus Folk's classification (figures below) is most suited for thin section study. Remember that he terms rocks with appreciable matrix as micrites while matrix-free rocks that contain sparry calcite cement are termed sparites. As you can see sparites and micrites are further subdivided by means of their most common grains.



Figure 1: Folk's Basic Classifications [1]



Figure 2: Folk's Textural Classifications [1]

In contrast, Dunham's classification (figures below) and its modification by Embry and Klovan (1971) and James (1984) deal with depositional texture. For this reason, his scheme may be better suited for rock descriptions that employ a hand lens or binocular microscope. For example, if the grains of a limestone are touching one another and the sediment contains no mud, then the sediment is called a grainstone. If the carbonate is grain supported but contains a small percentage of mud, then it is known as a packstone. If the sediment is mud supported but contains more than 10 percent grains, then it is known as a wackestone, and if it contains less than 10 percent grains and is mud supported, it is known as a mudstone.

Original con	nponents not b			
(particles	Contains mud of clay and fin	Original components bound together at deposition. Intergrown		
Mud-su	pported	skeletal material, lamination contrary to gravity or cavities		
Less than 10% Grains	More than 10% Grains			floored by sediment, roofed over by organic material but too large to be interstices
Mudstone	Wackestone	Packstone	Grainstone	Boundstone

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

Figure 3: Dunham's Classifications [1]

Allocht	honous	Autochthonous					
Original com bound orga depos	ponents not anically at ition	Original organi	Original components bound organically at deposition				
>10%grair	is>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			
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		KXXX KXXX	K K Kol				

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

Figure 4: Dunham's Reef Limestone Classifications [1]

#### 2.2 Hydrochloric Acid [2]

Hydrochloric acid is a solution of hydrogen chloride (HCl) in water, that is a highly corrosive, strong mineral acid with many industrial uses. Historically called muriatic acid or spirits of salt, hydrochloric acid was produced from vitriol (sulfuric acid) and common salt.

Hydrochloric acid is a monoprotic acid, which means it can dissociate (*i.e.*, ionize) only once to give up one  $H^+$  ion (a single proton). In aqueous hydrochloric acid, the  $H^+$  joins a water molecule to form a hydronium ion,  $H_3O^+$ :

 $HCI + H_2O \rightarrow H_3O^+ + CI^-$ 

The other ion formed is Cl<sup>-</sup>, the chloride ion. Hydrochloric acid can therefore be used to prepare salts called *chlorides*, such as sodium chloride. Hydrochloric acid is a strong acid, since it is essentially completely dissociated in water.

Of the six common strong mineral acids in chemistry, hydrochloric acid is the monoprotic acid least likely to undergo an interfering oxidation-reduction reaction. Intermediate-strength hydrochloric acid solutions are quite stable upon storage, maintaining their concentrations over time. These attributes, plus the fact that it is available as a pure reagent, make hydrochloric acid an excellent acidifying reagent.

#### 2.3 Formic Acid [3]

Formic acid (also called methanoic acid) is the simplest carboxylic acid. Its chemical formula is CH<sub>2</sub>O<sub>2</sub>. It is an important intermediate in chemical synthesis and occurs naturally, most notably in the venom of bee and ant stings. In fact, its name comes from the Latin word for ant, *formica*, referring to its early isolation by the distillation of ant bodies.

Formic acid is a colorless liquid having a highly pungent, penetrating odor at room temperature. It is miscible with water and most polar organic solvents, and is somewhat soluble in hydrocarbons. In hydrocarbons and in the vapor phase, it consists of hydrogen-bonded dimers rather than individual molecules. Heat and especially acids cause formic acid to decompose to carbon monoxide (CO) and water (dehydration). Treatment of formic acid with sulfuric acid is a convenient laboratory source of CO.

#### 2.4 Acid Dissociation Constant

Acid dissociation constant,  $K_a$ , (also known as acidity constant, or acid-ionization constant) is a quantitative measure of the strength of an acid in solution. It is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions. The equilibrium can be written symbolically as:

 $HA \rightleftharpoons A^- + H^+$ 

where HA is a generic acid that dissociates by splitting into A<sup>-</sup>, known as the conjugate base of the acid, and the hydrogen ion or proton, H<sup>+</sup>, which, in the case of aqueous solutions, exists as a solvated hydronium ion. [4]

Due to the many orders of magnitude spanned by  $K_a$  values, a logarithmic measure of the acid dissociation constant is more commonly used in practice. The logarithmic constant,  $pK_a$ , which is equal to  $-\log_{10} K_a$ , is sometimes also (but incorrectly) referred to as an acid dissociation constant:

 $pK_{\rm a} = -\log_{10}K_{\rm a}$ 

The larger the value of  $pK_a$ , the smaller the extent of dissociation. A weak acid has a  $pK_a$  value in the approximate range -2 to 12 in water. Acids with a  $pK_a$  value of less than about -2 are said to be strong acids; a strong acid is almost completely dissociated in aqueous solution, to the extent that the concentration of the undissociated acid becomes undetectable. [5]

#### 2.5 Acidizing Experiments [6]

Matrix acidizing experiments combined with visualization techniques is the common method used to study the details of worm-hole networks formed during matrix acidizing of carbonate reservoir rock. Results from these experiments provided much extensive information on one dimensional wormhole growth along with some basic information of two dimensional growth mechanisms. However, if three dimensional wormhole characteristics are to be understood, large-scale test systems must be considered.

This study introduced a newly developed method that integrates acidizing experiments on carbonate rock samples. This method can analyze up t 14 ft cube of carbonate rock in volume. It also includes high-resolution nondestructive imaging and analysis and computational modeling to extend the results to field applications. In these large-scale tests, carbonate rock samples with varying mineralogy and pore structure are evaluated experimentally by use of open-hole or cased-and-perforated completions configurations.



Figure 5: Schematic of large Acidizing Cell [6]



Figure 6: Top view of wormhole structure [6]



Figure 7: Side view of wormhole structure [6]

#### 2.3 Kinetics Dissolution of Carbonates

Kinetics dissolution is generally the rate of dissolution. In this project, the study on carbonate kinetics dissolution is done in order to find out the rate of dissolution when they are exposed to certain chemicals. In this case, the chemicals are two different types of diluted acid which are hydrochloric acid and formic acid.

Water at the surface of the earth inevitably contains dissolved CO2, either as a result of equilibration with the atmosphere or because of respiration by organisms. CO2 reacts with water to form carbonic acid [CO2 + H2O  $\leftrightarrow$  H2CO3] and some of the carbonic acid dissociates to form bicarbonate and hydrogen ions [H2CO3  $\leftrightarrow$  H+ + HCO3-]. Some of the bicarbonate will dissociate to an additional hydrogen ion and a carbonate ion [HCO3-  $\leftrightarrow$  H+ + CO3 2-]. [15]

The importance of the carbonate system is that by dissociating and providing hydrogen ions to solution, or associating and taking up free hydrogen ions, it controls the pH of many natural waters. [8] In addition, calcite and other carbonates are extremely common minerals in soils and in sedimentary, metamorphic, and altered igneous rocks. [9] Ground waters will tend to approach equilibrium with calcite by either dissolving it or precipitating it. [13, 14] The dissolution activity of the carbonate ion had been identified to be very low at pH 6.35.

## METHODOLOGY

3.1 Research Methodology

Below is the methodology and general flow of this project:



Figure 8: Flow Chart of the Project

- 3.2 Tools
  - Coring Machine
  - Rock Cutting Machine
  - Trimming Machine
  - Precision Cutter
  - Lapping and Polishing Machine



Figure 9: Coring Machine Figure 10: Lapping & Polishing Machine



Figure 11: Cutting Machine

- Experiment Apparatus
  - 1. Beaker to contain acid and core samples.
  - 2. PH Meter to measure the pH of the acids after the dissolutions.
  - 3. Heating Oven- to dry the core samples before the weight is taken.
  - 4. Digital Weight Scale- to weight the samples after dissolutions.



Figure 12: Digital Weight Scale



Figure 13: pH Meter

### 3.3 Project Activities

### Samples collection

There are two samples that had been used in this study. The first sample is from Batu Gading and another one is from Bukit Niah. Both samples originated from Sarawak. Batu Gading sample was taken from a quarry and it is filled with Nummulite fossils. Since the samples will be immerse in two types of acids with each of them have two different molarities, the results obtained are different.



Figure 14: Sample from Batu Gading, Sarawak



Figure 15: Sample from Bukit Niah (Subis Limestone), Sarawak

Core Sampling

Procedure for core sampling:

- One core plug cored from each sample using the coring machine. (diameter = 1.5 inches)
- 2. Each core was cut to 2 pieces. (thickness = 2cm)



Figure 16: Core Sample from Batu Gading (Left), & Bukit Niah (Right)

Experiment Procedures



Figure 17: Setup for both samples

- 1. Prepare all the required apparatus.
- 2. Prepare 2 core samples from each of the two sample types and clean them thoroughly.
- 3. Measure the weight of each core samples as initial measurement.
- Fill 2 beakers with 0.1M HCL, and 2 beakers with 0.1M formic acid. (Volume of acid = 75ml)
- 5. Put 1 core samples from each sample type into the each beaker with hydrochloric acid and another 2 core samples into the beakers with formic acid.

- 6. Pick the core samples up after 5 minutes and dry the samples in heating oven before measuring the weight as measurement at first 5 minutes.
- 7. Check the pH and the volume of the remaining acids and transfer the acids into test tubes.
- 8. Pour 75ml of acid into each beaker.
- 9. Repeat step 6 to 8 every 15 minutes for the next 5 hours.
- 10. Note down all measurements in a table.



Figure 18: Experiments Setup

### 3.3 Gantt Chart& Key Milestones

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15	16
1	Briefing & update on student progress																	
2	Project work commences			NI ST									T. T. S		-			
3	3 Submission of Progress Report																	
4	PRE-SEDEX Poster Exhibition								break									
5	SEDEX	_							nester									
6	Draft Report Submission	_							Aid-sen	-								
7	Dissertation Submission																	
8	Technical Paper Submission	_																
9	Oral Presentation		-						-									
10	Project Dissertation Submission	-							-									

Planned Task: Completed Task:



## **RESULTS & DISCUSSIONS**

• Data for sample from Batu Gading, Sarawak in 0.1M HCL.

### Table

Time			Weight (g)	рН
	Before	After	Cumulative Weight Loss	After
5 min.	58.8	58.78	0.02	1.13
10 min.	58.78	58.75	0.05	1.14
15 min.	58.75	58.72	0.08	1.18
30 min.	58.72	58.62	0.18	1.36
45 min.	58.62	58.53	0.27	1.40
1 hr.	58.53	58.46	0.34	1.43
2hr.	58.46	58.12	0.68	2.24
3hr.	58.12	58.06	0.74	2.59
4hr.	58.06	58.003	0.79	2.84
5hr.	58.003	57.96	0.84	4.37

Figure 19: Data table for Batu Gading sample. (0.1M HCL)

## Graphs



Figure 20: Weight vs Time Graph (Batu Gading 0.1M HCL)



Figure 21: pH vs Time Graph (Batu Gading 0.1M HCL)



Figure 22: Cumulative Weight Loss vs Time Graph (Batu Gading 0.1M HCL)

For sample from Batu Gading in 0.1M HCL, the initial weight of the core sample is 58.8g and the final weight after 5 hours of dissolution is 57.96. pH values for 0.1M HCL increase slowly from 5 minutes to 1 hour, but from 1 hour to 5 hours, the values increase significantly from 1.43 to 4.37.

The cumulative weight loss of the sample increase slowly from 5 minutes to 1 hour, but from 1 hour to 2 hours, it increases dramatically from 0.34g to 0.68g. The total weight loss for this sample after 5 hours is 0.84g Data for sample from Bukit Niah, Sarawak in 0.1M HCL.

## Table

Time		V	Veight (g)	рН
	Before	After	Cumulative Weight Loss	After
5 min.	58.90	58.89	0.01	1.21
10 min.	58.89	58.86	0.03	1.22
15 min.	58.86	58.77	0.13	1.25
30 min.	58.77	58.68	0.22	1.29
45 min.	58.68	58.51	0.39	1.36
1 hr.	58.51	58.43	0.47	1.41
2hr.	58.43	58.36	0.54	2.16
3hr.	58.36	58.28	0.62	2.48
4hr.	58.28	58.20	0.70	2.75
5hr.	58.20	58.13	0.77	3.12

Figure 23: Data table for Bukit Niah sample. (0.1M HCL)

## Graphs



Figure 24: Weight vs Time Graph (Bukit Niah 0.1M HCL)



Figure 25: pH vs Time Graph (Bukit Niah 0.1M HCL)





For sample from Bukit Niah in 0.1M HCL, the initial weight of the core sample is 58.9g and the final weight after 5 hours of dissolution is 58.13. pH values for 0.1M HCL increase slowly from 5 minutes to 1 hour, but from 1 hour to 5 hours, the values increase significantly from 1.41 to 3.12.

The cumulative weight loss of the sample increase slowly from 5 minutes to 15 minutes, but from 15 minutes to 5 hours, it increases steadily from 0.13g to 0.77g. The total weight loss for this sample after 5 hours is 0.77g

Data for sample from Batu Gading, Sarawak in 0.1M Formic Acid.

## Table

Time		рН		
	Before	After	Cumulative Weight Loss	After
5 min.	59.52	59.51	0.01	2.18
10 min.	59.51	59.48	0.03	2.25
15 min.	59.48	59.46	0.06	2.37
30 min.	59.46	59.28	0.24	2.69
45 min.	59.28	59.16	0.36	3.04
1 hr.	59.16	59.04	0.48	3.42
2hr.	59.04	58.97	0.55	3.61
3hr.	58.97	58.89	0.63	3.73
4hr.	58.89	58.83	0.69	3.79
5hr.	58.83	58.74	0.78	3.86

Figure 27: Data table for Batu Gading sample. (0.1M Formic Acid)

## Graphs



Figure 28: Weight vs Time Graph (Batu Gading 0.1M Formic Acid)



Figure 29: pH vs Time Graph (Batu Gading 0.1M Formic Acid)





For sample from Batu Gading in 0.1M Formic Acid, the initial weight of the core sample is 59.52g and the final weight after 5 hours of dissolution is 58.74g. pH values for 0.1M Formic Acid increase steadily from 5 minutes to 1 hour, but from 1 hour to 5 hours, the values increase slowly from 3.42 to 3.86.

The cumulative weight loss of the sample increase slowly from 5 minutes to 15 minutes, but from 15 minutes to 5 hours, it increases steadily from 0.06g to 0.78g. The total weight loss for this sample after 5 hours is 0.78g

• Data for sample from Bukit Niah, Sarawak in 0.1M Formic Acid.

## Table

Time		рН		
	Before	After	Cumulative Weight Loss	After
5 min.	59.39	59.37	0.02	2.18
10 min.	59.37	59.36	0.03	2.25
15 min.	59.36	59.35	0.04	2.4
30 min.	59.35	59.26	0.13	2.62
45 min.	59.26	59.16	0.23	2.94
1 hr.	59.16	59.02	0.37	3.16
2hr.	59.02	58.93	0.46	3.59
3hr.	58.93	58.86	0.53	3.65
4hr.	58.86	58.77	0.62	3.75
5hr.	58.77	58.68	0.71	3.82

Figure 31: Data table for Bukit Niah sample. (0.1M Formic Acid)





Figure 32: Weight vs Time Graph (Bukit Niah 0.1M Formic Acid)



Figure 33: pH vs Time Graph (Bukit Niah 0.1M Formic Acid)



#### Figure 34: Cumulative Weight Loss vs Time Graph (Bukit Niah 0.1M Formic Acid)

For sample from Bukit Niah in 0.1M Formic Acid, the initial weight of the core sample is 59.39g and the final weight after 5 hours of dissolution is 58.68. pH values for 0.1M Formic Acid increase steadily from 5 minutes to 2 hours, but from 2 hours to 5 hours, the values increase slowly from 3.59 to 3.82.

The cumulative weight loss of the sample increase slowly from 5 minutes to 15 minutes, but from 15 minutes to 5 hours, it increases steadily from 0.04g to 0.71g. The total weight loss for this sample after 5 hours is 0.71g

Based on the cumulative weight loss of both samples, we can see that sample from Batu Gading is higly soluble in 0.1M HCL with 0.84g loss in weight compare to sample from Bukit Niah which is only 0.77g. It is also the same when the samples are immersed in 0.1M Formic Acid where sample from Batu Gading loss 0.78g and sample from Bukit Niah loss 0.71g.



Figure 35: Dissolution Rate vs Time Graph (All Samples)

Above is the dissolution rate vs time graph for all samples. As we can see, the dissolution rate for all samples increased from 5 minutes to 1 hour. However, after the 1<sup>st</sup> hour until the 5<sup>th</sup> hour, the dissolution rate decreased. There are several occasional peak on the graph where the dissolution rate increases. This is due to the fabric variationsof the samples surface.

Both samples loss more weight after the first hour of the experiments because from time to time, when the acid dissolve the carbonates, it will create new pore spaces thus increasing the surface area that will come in contact with the acid.

If we compare the pH of 0.1M HCL and 0.1M Formic Acid for both samples throughout the experiment, we can see that pH value for 0.1M Formic Acid increase faster compared to 0.1M HCL. This is because; the value of acid dissociation constant (pKa) for Formic Acid is only 3.75 compared to HCL.

## SEM

Both samples were observed under a Scanning Electron Microscope (SEM). This is done so that the differences of the surface particles between both samples can be compared.



Figure 36: Batu Gading sample (5000 times magnification)



Figure 37: Bukit Niah sample (5000 times magnification)

As we can see from figure 36 & 37, the particles size of Batu Gading sample is much smaller compared to Bukit Niah sample. This is one of the main reasons Batu Gading sample has higher weight loss compared to Bukit Niah sample because smaller particles size will create more surface area for the acid dissolve the rock.

Furthermore, sample from Batu Gading also have more pores and tiny holes compared to sample from Bukit Niah. This will allows the acid to penetrate deeper into the rock thus increasing the dissolution rate of the rock.

## CONCLUSIONS

It has been shown that the high surface area of the rock sample creates greatly enhanced apparent dissolution rates. Theoretically, at constant temperature, increasing the pH increased dissolution rate, whereas at constant pH, dissolution rate increases with temperature.

From this experiment, it can be concluded that the carbonates will have higher dissolution rate in inorganic acids compare to organic acids. This is mainly because inorganic acid have higher value of acid dissociation constant (pKa) compared to organic acid.

### RECOMMENDATION

From this project, we know that dissolution rate of the carbonates are different in several types of acids. This is because; each type of acid has its own strength in terms of its value of acid dissolution constant (pKa). For future projects, the experiments should be done with other acids so that the dissolution rate of the carbonates can be identified.

Other recommendation for this project is to run the experiment with several types of additives. In the industry, the additives are used during acidizing in order to achieve deeper penetration. Some of the additives that are widely used are Calcium Chloride  $(CaCl_2)$ , Carbon Dioxide  $(CO_2)$ , and also Acetic Acid. With the additives, we can identify the effects of it towards the kinetics dissolution of the carbonates in acids.

### REFERENCES

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