FEASIBILITY STUDY ON MATRIX ACIDIZING OF NORTHEASTERN THAILAND PERMIAN LIMESTONE BY USING HYDROCHLORIC ACID

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A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Civil, Transportation and Geo-Resources Engineering

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การศึกษาความเป็นไปได้ในการละลายเนื้อหินด้วยกรดของหินปูน ยุคเพอร์เมียนในภาคตะวันออกเฉียงเหนือของประเทศไทย โดยใช้กรดไฮดรอคลอริก

นายวรชิต นาคพงษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมโยธา ขนส่ง และทรัพยากรธรณี

มหาวิทยาลัยเทคโนโลยีสุรนารี

ปีการศึกษา 2562

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Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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การวิจัยครั้งนี้มีวัตถุประสงค์เพื่อศึกษาประสิทธิภาพของความเข้มข้นของกรดไฮดรอคลอริกต่อการเปลี่ยนแปลงสมบัติทางกายภาพของหินปูนยุคเพอร์เมียนในภาคตะวันออกเฉียงเหนือของประเทศไทย ตัวอย่างหินปูนได้ถูกรวบรวมมาจากหมวดหินผานกเค้า หมวดหินน้ำมโหฬาร และหมวดหินเขาขาด ตัวอย่างหินได้ถูกแช่ไว้ 24 ชั่วโมง ในสารละลายกรดไฮดรอคลอริกที่มีความเข้มข้นร้อยละ 5 10 15 และ 20 ภายใต้อุณหภูมิห้อง การศึกษาธาตุและแร่ประกอบของหินปูนตัวอย่างได้ถูกทำการวิเคราะห์ด้วยเครื่องวิเคราะห์การเลี้ยวเบนรังสีเอกซ์ (XRD) และเครื่องวิเคราะห์โดยวิธีเอกซเรย์ฟลูออเรสเซนต์ (XRF) ตามลำดับ ผลการทดสอบพบว่าปริมาณของแร่แคลไซต์ ($CaCO_3$) และปูนขาว (CaO) นั้นเป็นสัดส่วนโดยตรงต่อปริมาณของค่าความพรุนและอัตราการละลายของเนื้อหินปูน ในการศึกษาครั้งนี้ปริมาณของค่าความพรุนและสัณฐานวิทยาของโครงสร้างขนาดไมโครของเนื้อหินได้ถูกทำการวิเคราะห์โดยใช้เครื่องวัดความพรุนและโดยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) ผลการศึกษาพบว่าปริมาณและขนาดของโพรงขนาดไมโครของหินตัวอย่างนั้นเพิ่มขึ้นเมื่อความเข้มข้นของกรดไฮดรอคลอริกนั้นเพิ่มขึ้นและกรดไฮดรอคลอริกที่มีความเข้มข้นร้อยละ 15 นั้นเป็นค่าความเข้มข้นที่มีความเหมาะสมที่สุดในการทำการละลายเนื้อหินปูนยุคเพอร์เมียนในภาคตะวันออกเฉียงเหนือของประเทศไทย

สาขาวิชาเทคโนโลยีธรณี ลายมือชื่อนักศึกษา________

ปีการศึกษา 2562 ลายมือชื่ออาจารย์ที่ปรึกษา________

WORACHIT NAKPONG : FEASIBILITY STUDY ON MATRIX ACIDIZING OF NORTHEASTERN THAILAND PERMIAN LIMESTONE BY USING HYDROCHLORIC ACID. THESIS ADVISOR : ASST. PROF. BANTITA TERAKULSATIT, Ph.D., 101 PP.

MATRIX ACIDIZING/POROSITY/DISSOLUTION/PETROGRAPHY

The objective of this research is to study the efficiency of the concentration of hydrochloric acid (HCl) on the physical property change of northeastern Thailand Permian limestone. The limestone samples were collected from Pha Nok Khoa, Nam Mahoran, and Khao Khad Formation. These rock samples were 24 hours soaked in 5 10 15 and 20% HCl concentration under the room temperature. The elemental and mineral composition of the limestone samples were analyzed by X-ray fluorescence (XRF) and X-ray diffraction (XRD) respectively. Test results indicated that calcite ($CaCO_3$) and lime (CaO) contents was directly proportional to the quantity of porosity and the rate of limestone matrix dissolution. In this study, the quantity of porosity and the morphology of the rock matrix microstructure were also analyzed by the Porosimeter and the Scanning Electron Microscope (SEM). Results of the study indicated that the quantity and the size of rock sample micropores increased with the HCl concentration increasing and the HCl 15% concentration was the most suitable for conducting the matrix acidizing of northeastern Thailand Permian limestone.

School of Geotechnology | Student's Signature Worachit

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SYMBOLS AND ABBREVIATIONS

HCL	=	Hydrochloric
SEM	=	Scanning Electron Microscope
XRF	=	X-ray fluorescence
XRD	=	X-ray diffraction
µm	=	Micrometer
mm	=	Millimeter
cm	=	Centimeter
Temp.	=	Temperature
M	=	Mole
θ	=	Theta
º	=	Degree
RV	=	Reference Volume
PV	=	Pore Volume
GV	=	Grain Volume

CHAPTER I

INTRODUCTION

1.1 Rationale and background

Thailand's petroleum resources have declined due to the long-term production and the major onshore of petroleum is found in the northeastern part of the country. The characteristics of the reservoirs are divided into 2 types: 1) Clastic Reservoir 2) Carbonate Reservoir and the problems found in the carbonate reservoir are manifold and varied (heterogeneous) like porosity, permeability, etc cause problems during production. Acidizing has been used to help improve the properties of the reservoir this is usually done in conjunction with hydraulic fracturing. Therefore, the study on the efficiency of the concentration of hydrochloric acid on the dissolution of limestone and observe the physical and chemical changes before and after using hydrochloric acid. It will be possible to determine the suitability of the hydrochloric acid concentration to improve the permeability and porosity of the reservoir. The initial concentration was used in the carbonate reservoir in the other formations in northeastern Thailand and it also helps to reduce the cost of propping agents.

1.2 Research objectives

1.2.1 To study the chemical and physical properties of the Permian limestone in Northeastern Thailand.

1.2.2 To study the efficiency of hydrochloric (HCl) acid concentration on the dissolution of limestone.

1.2.3 To determine the porosity of limestone both before and after dissolve with HCl.

1.3 Scopes and limitations of the study

This research aimed to investigate the chemical and physical properties of limestone in northeast Thailand. The physical and chemical properties are operated at the laboratory of Suranaree University of Technology following:

1.3.1 Permian limestone in the northeastern part of Thailand consists of Saraburi group including Pha Nok Khao, Nam Mahoran, and Khao Khad Formation.

1.3.2 A chemical composition analyzed the mineral composition by using X-ray diffractometer (XRD), and the elemental composition by using X-ray fluorescence (XRF).

1.3.3 Physical properties such as porosity tested by “Porosimeter”

1.3.4 The morphology of the microstructure of limestone was analyzed by using the scanning electron microscope (SEM) to determining the primary and secondary porosity.

1.3.5 The efficiency of dissolution was tested by a concentration of 5%, 10%, and 15% hydrochloric acid for 24 hr.

1.3.6 The sample rock was dissolved in a single dissolution and was not reused.

1.3.7 The characteristic of limestone is heterogeneous rocks.

1.3.8 All the investigations will test at ambient conditions.

1.4 Thesis contents

Chapter I introduces the thesis by briefly describing the background of the problem and the significance of the study. The research objectives, scope, and limitations are identified. **Chapter II** summarizes the results of the literature review to improve an understanding of Permian limestone in Northern Thailand and the factor that effects of Carbonate acidizing. **Chapter III** describes the sample preparation and the experimental procedure for laboratory tests. **Chapter IV** presents the results obtained from the laboratory tests and a comparison of the results between each mud formula. **Chapter V** discusses and concludes the research results and provides recommendations for future research studies.

CHAPTER II

LITERATURE REVIEW

2.1 General geology of northeastern Thailand

Chonglakmani (1984) classified Permian rocks in Thailand of Saraburi groups in the area of Phetchabun, Nong Bua Lamphun, Chaiyaphum and Khon Kaen province there are 3 formations including Pha Nok Khao Formation, Hua Na Kham Formation, and Nam Duk Formation. Phylloid algae are a prominent component of carbonate facies comprising the Pha Nok Khao (PNK) and contemporaneous Khao Khwang platforms of the Loei-Phetchabun Foldbelt in northeastern Thailand as shown in Figure 2.1.

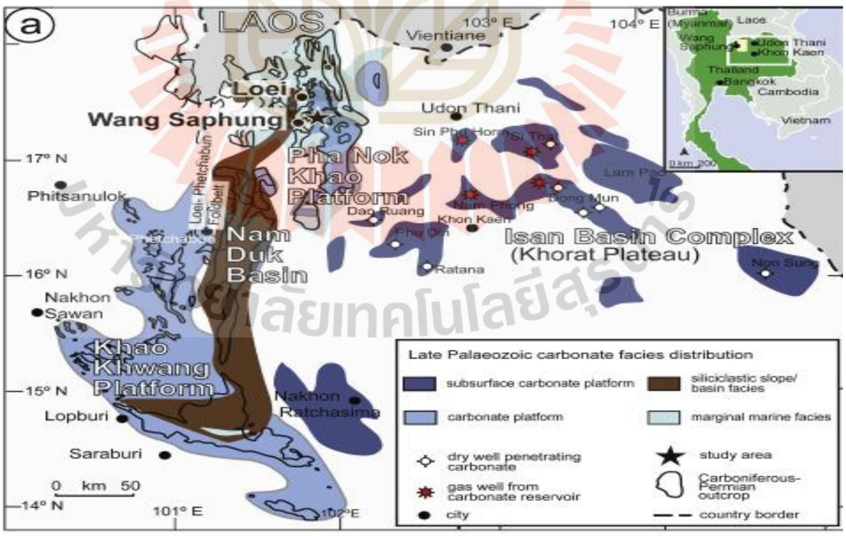


Figure 2.1 Geological of the Loei-Phetchabun Foldbelt in northeastern Thailand (Chonglakmani, 1984).

Charoenprawat et al. (1984) classified Saraburi groups (P) in the area of Loei province there is 3 formations such as Nam Mahoran Formation (P1), E-Lert Formation (P2), and Pha Dua Formation (P3) in order from bottom to top as shown in Figure 2.2.

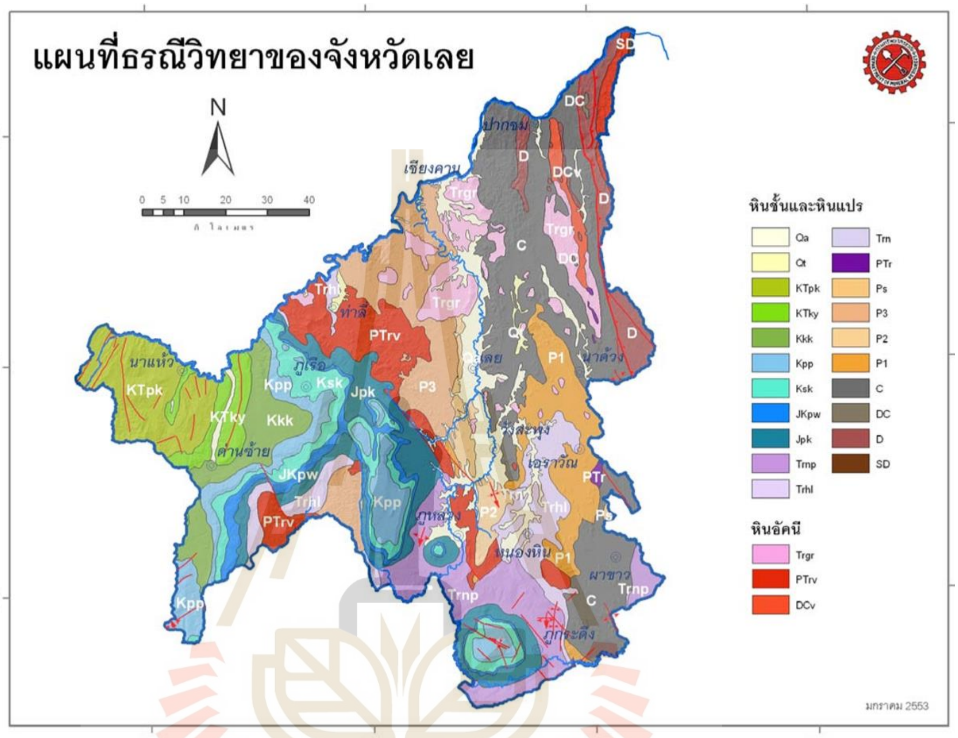


Figure 2.2 Geologic map of Loei Province (Department of Mineral Resources, 2012).

Hinthong et al. (1985) classified Permian limestone in the area of Saraburi, the boundary with Lopburi and Nakhon Ratchasima Province there is 6 formations including Phu Phe Formation, Khao Khwang Formation, Nong Pong Formation, Pang Asok Formation, Khao Khad Formation, and Sap Bon Formation in order from bottom to top as shown in Figure 2.3.

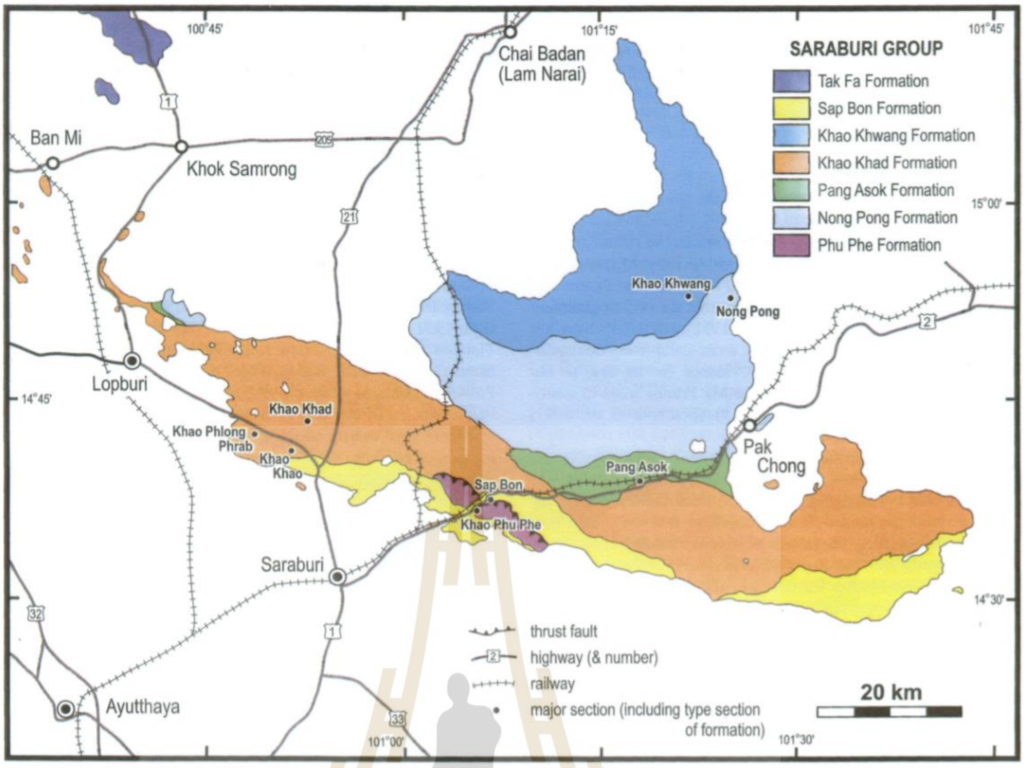


Figure 2.3 Geologic map of Saraburi Province (Ridd et al., 2011).

Chonglakmani (2005) studied the Permian Saraburi Group, distributed from Amphoe Muak Lek of Changwat Saraburi and Amphoe Pak Chong of Changwat Nakhon Ratchasima to Amphoe Lom Sak of Changwat Phetchabun1 (Table 2.1). The first lithofacies is thin- to thick- bedded bioclastic limestone and dolomite. The limestones are high purity, and composed mainly of calcite, and are partly recrystallized. Part of limestones is lower purity because of the replacement of calcite by chert or dolomite. The second lithofacies is coral- algal boundstone with the composed mainly of corals and calcareous algae. Other lithologic types are medium-bedded to thick-bedded to massive floatstone and rudstone. The Khao Phang Ma Formation consists of crinoidal limestone, micritic limestone, and shale. The limestones are and lenticular hummocky cross-bedded, consisting mainly of calcite. But they are rather low in purity due to the interbedded shale beds. The assessment of limestone resources of the study area is based on the chemical analysis, brightness analysis and mechanical analysis of the collected limestone sample.

Table 2.1 The classification of Saraburi group accumulated in Saraburi Province and nearby (Chonglakmani, 2005).

Ma				Thailand	Khao Khwang Platform - Basin		Phetchabun Fold Belt	
Triassic	250	Lower	Griesbachian		Saraburi	Pak Chong	Lom Sak	
Permian		Lopingian	Changxingian	Dorashamian				
	260		Wuchiapingian	Dzhulfian				
		Guadalupian	Capitanian	Midian	Sap Bon Fm.		Nam Nao Fm. (Molasse)	
			Wordian	Murgabian	Khao Phaeng Ma Fm.	Pang Asok Fm.	(Flysch)	
	270		Roadian					
	280	Cis-Uralian	Kungurian	Kubergndian Bolorian	Khao Khwang Fm.	Nong Pong Fm.	(Pelagic)	Nam Duk Fm.
			Artinskian	Yakhtashian				
	290		Sakmarian	Sakmarian				
			Asselian	Asselian				
Carbonif.	300	Upper	Gzhelian					

Chonglakmani et al. (1978) conclude the stratigraphy of Phetchabun, Nong Bua Lamphun, Chaiyaphum, and Khon Kaen provinces consisting of three formations including Pha Nok Khao Formation, Hua Na Kham Formation, and Nam Duk Formation as shown in Figure 2.4. The gas reservoir of Khorat Plateau Basin, northeastern Thailand produced from both non-marine clastic and shallow-marine carbonate reservoirs. The Pha Nok Khoa Platform is composed of two main facies rocks including carbonate and siliciclastic. The Pha Nok Khao Formation is characterized by the massive bed of gray limestone facies with some nodular and lenticular chert. Fossils assemblages are included fusulinids and corals that indicate the Early to the Middle Permian in age.

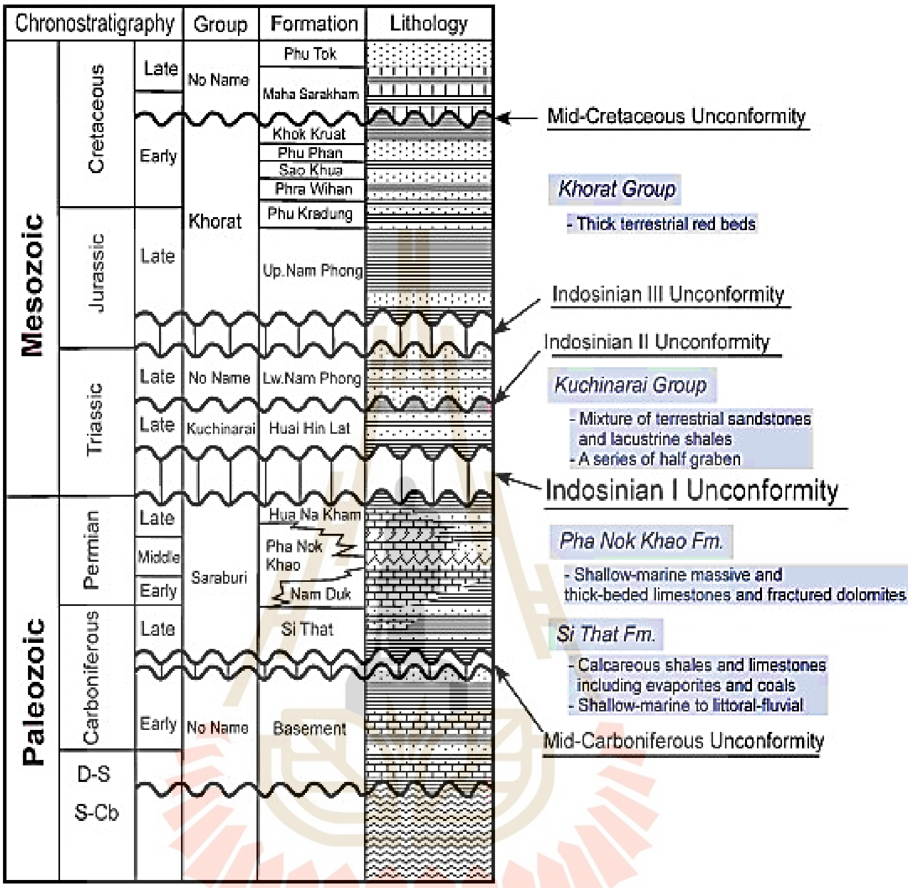


Figure 2.4 Stratigraphy of Saraburi groups in Chaiyaphum province.

Ueno et al. (2011) studied stratigraphy of Saraburi, Lopburi, and Pak Chong district in Nakhon Ratchasima provinces consisting of six formations including Sap Bon Formation, Khao Khad Formation, Pang Asok Formation, Nong Pong Formation, Khao Khwang Formation, and Phu Phe Formation. The carbonate is produced from a marine platform to the basin environment. The zone using fusulinid, in contrast to the conodonts being the primary fossil used for the biostratigraphic correlation for The

International Commission on Stratigraphy (ICS) Permian Timeline as shown in Figure 2.5.

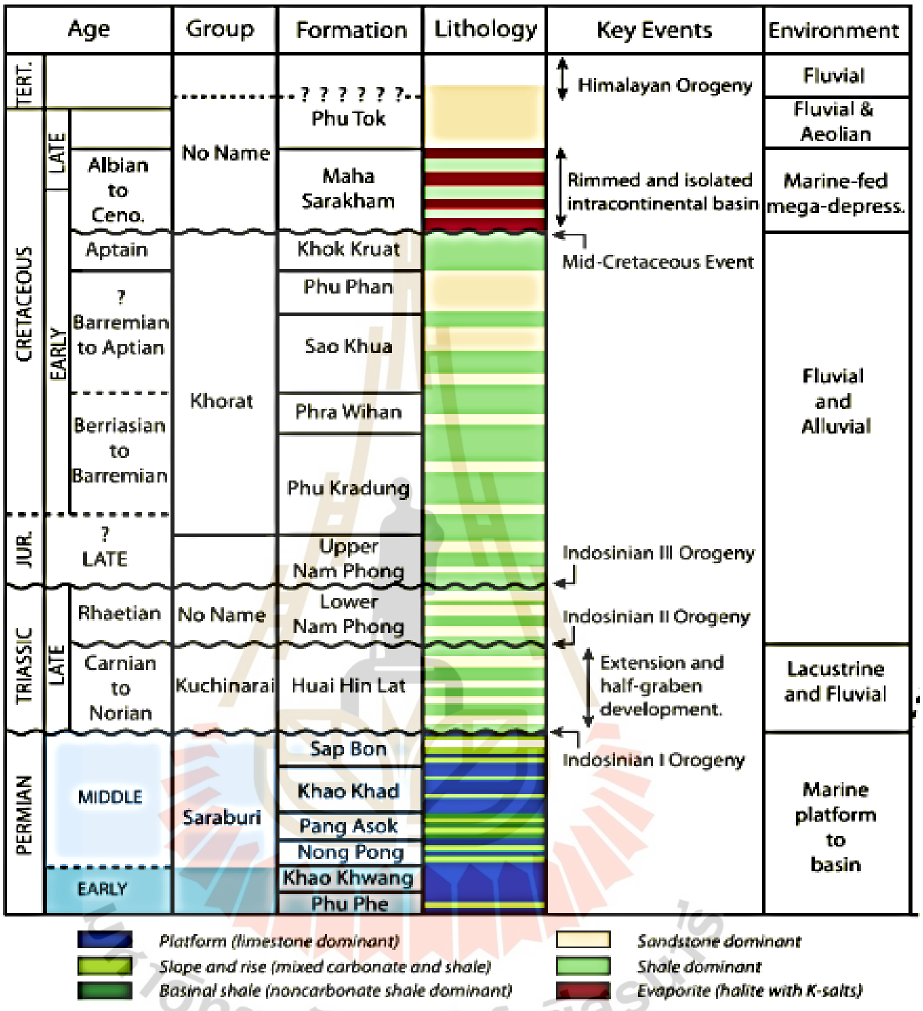


Figure 2.5 Stratigraphy of Saraburi groups in Pak Chong district, Nakhon Ratchasima province (Hinthong et al., 1985).

Ueno et al. (2011) stratigraphy of Saraburi Group in the Loei Fold-belt includes four main formations (Figure 2.6) including Wang Saphung Formation, Nam Mahoran Formation, E-Lert Formation, and Pha Dua Formation. The fossil assemblage within the Nam Mahoran Formation consists of the abundant crinoids, diverse algal assemblages, fusulinids, corals, bivalves, calcisponges, and small foraminifera, which represented a tropical Permian environment.

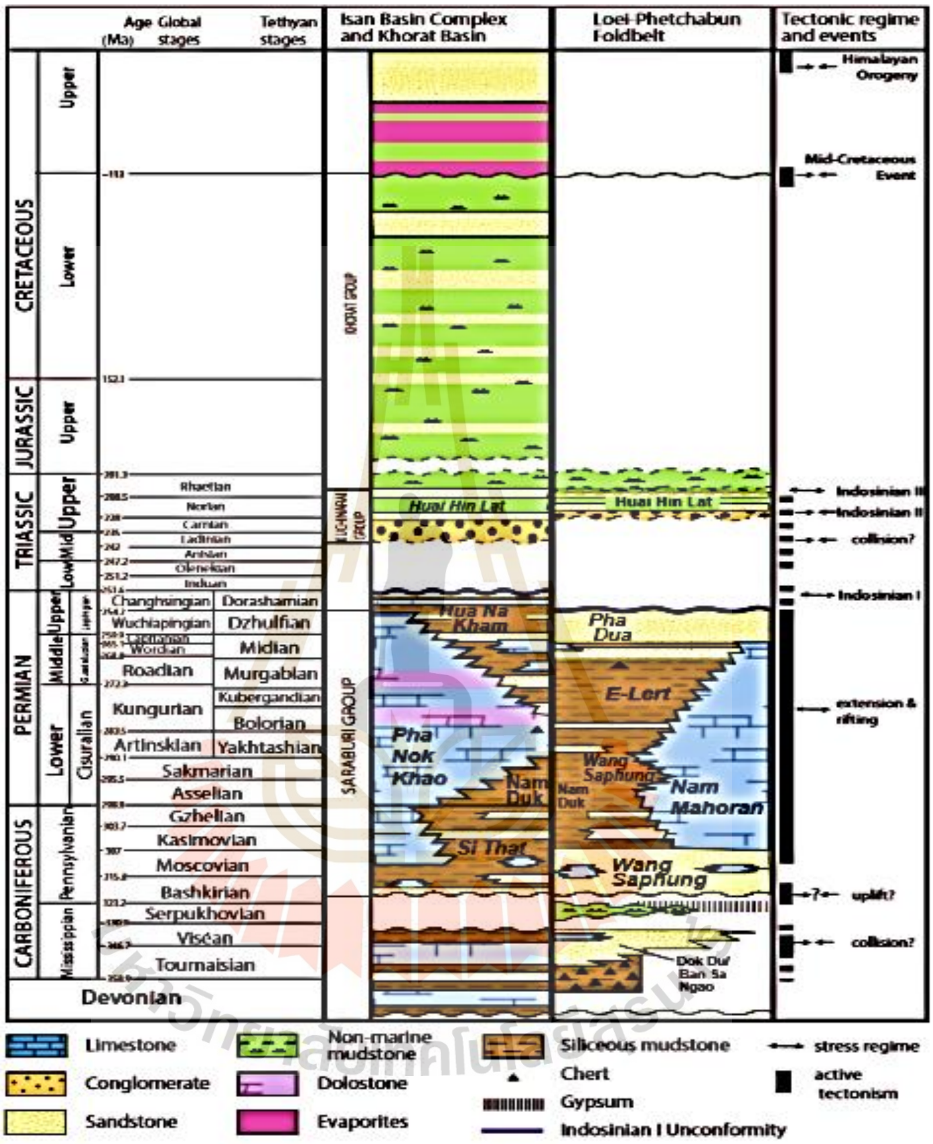


Figure 2.6 Tectono-stratigraphic summary comparing the Loei-Phetchabun Fold belt and the Khorat region (Ueno et al., 2011).

Esso (1982) reported that the significant gas discovery in Nam Phong Field. The well was drilled to test the potential of the section below what was then and subsequently referred to as the Base Khorat Unconformity, today renamed the Indosinian II Unconformity. It was proposed from outcrop studies and the results of Kuchinarai-1, that this section would contain Saraburi Group carbonates, acting as the reservoir target, and lacustrine, oil-prone source rocks in the Kuchinarai Group preserved around the flanks of the structure. At the time it was felt that this was an oil play, although a high level of maturity of the source-rocks was anticipated and gas, for which there was no market, was a recognized commercial risk. Data on this field has been kept proprietary by the operator, however, some idea of their play concepts and factual information can be gathered from Kozar et al. (1992). It is known that the well encountered overpressure and gas shows in the lower part of the Khorat Group. It penetrated a thin section of Kuchinarai Group elastics, containing tight gas-charged sandstones, before entering a thick section of Pha Nok Khao Formation carbonates, below the Indosinian I Unconformity. Due to the overpressure in the overlying sections, the mud weight had been raised to somewhere in the order of 14 ppg, however, the top of the carbonates had been karstified, reportedly resulting in lost circulation problems. The carbonates proved to consist of upper and lower limestone units, with a thick intervening dolomite unit. The well reached a TD of around 4000m within the Si That Formation.

Booth (2005) in SEAPEX Exploration Conference 2005 presented Khorat Plateau Basin, NE Thailand, Discoveries, and Future Exploration Potential. The reservoir for this field is a Permian age platform carbonate (Pha Nok Khao Formation). Three appraisal wells were drilled on the Phu Horn gas field, which had been discovered by Esso in 1983 and also has a Permian platform carbonate reservoir. These wells were drilled underbalanced, with spectacular increases in production rates – the PH-1 well produced only 4 mmscf/d, whilst the recent wells have all been long term tested more than 30 mmscf/d. There is a proven hydrocarbon system in the basin that has charged Permian reservoirs with gas. The critical elements of this hydrocarbon system are the distribution and nature of the Permian carbonates, the source of the gas, and the timing of gas generation versus trap formation. The interplay of these critical elements that combine to make exploration plays in various parts of the basin are illustrated by a series of seismic sections.

Glumglomjit (2010) reviews about Carbonate reservoir characterization that, for the time being, Permian carbonates are the main gas-producing reservoir rocks in the northeastern region. The best reservoir rocks of this group are limestones and dolomites, especially dolomitized limestone, well-bedded dolomite, or the reefal origin. The rock units are coarsely crystalline and may have very high intracrystalline porosities. Various types of limestone such as fusulinid, crinoid calcarenites, oolite limestones, and the limestone reef bodies. Besides the matrix and vugular porosity, fractures are a very important parameter to enhance its reservoir quality.

Prididtan (1995) described the characteristics and properties of the Permian Carbonate reservoir are summarized as follows;

1) The carbonate was deposited on the platforms or related to the platforms. Lithofacies of the carbonates as observed in the core are mainly of fossiliferous packstone and grainstone with minor wackestone and mudstone.

2) The porosity and permeability of these carbonates are generally low. The porosity values range from 0 to 18 percent with an average matrix porosity of about 4.0 percent.

3) The Permian carbonates were deposited and buried at a great depth. They were subjected to many phases of karstifications and severe erosion.

4) The carbonates which contain high mud such as mudstone, and wackestone, have higher porosity values than those bearing a high grain such as packstone, grainstone, and boundstone. The dolomites have higher porosity than the limestones.

5) The permeability of the carbonate generally depends on the micro-fractures. The high flow rate of the Nam Phong gas field is related to the existence of open micro-fractures in limestone.

2.2 Chemical properties of limestone

Canham (1996) studied reservoir quality of Khorat Group in NE Thailand consists of a series of continental red-bed, divided here into five formations, which unconformably overlie the lithological-similar Nam Phong Formation. The reservoir quality of the Khorat Group data showed in Table 2.2.

Table 2.2 Summary of averaged petrographic data influencing reservoir potential, for the Khorat Group and Nam Phong Formation (Canham et al.,1996)

Formations	**Nam Phong**	**Phu Kradung**	**Phra Wihan**	**Sao Khua**	**Phu Phan**	**Khok Kruat**
Number of samples	18	19	14	12	14	12
Porosity	4.9 %	6.4 %	5.9 %	11.5 %	10.8 %	11.0 %
Primary	1.5 %	2.2 %	2.8 %	1.5 %	6.8 %	7.3 %
Secondary	3.2 %	3.0 %	2.5 %	8.0 %	3.3 %	2.5 %
Micro porosity	0.2 %	1.1 %	0.6 %	2.0 %	0.8 %	1.3 %
Silica	1.4 %	6.0 %	6.7 %	1.5 %	9.3 %	1.3 %
Calcite (ferroan and non-ferroan)	3.4 %	3.5 %	1.3 %	26.5 %	Absent	Absent
Kaolinite	0.3 %	2.1 %	4.1 %	2.0 %	1.8 %	Absent
Detrital clay	9.6 %	8.2 %	4.8 %	3.5 %	1.9 %	0.8 %

Shaikh et al. (1990) also collected data from Storugns. Table 2.3 shows the average results of the same elements as in Table 2.4, above. In addition to the main chemical components. Shaikh et al. (1990) also present data regarding trace elements and this is shown in Table 2.4 Overall Storugns has a very high CaO content (about 53 %) and low SiO_2 and Al_2O_3 (around 1.55 % and 0.76 % respectively). The magnesium levels are also relatively low (around 0.8 %) which is related to a low amount of dolomite and that the calcite is mostly low-mg calcite (Shaikh et al. 1990). There are also small amounts of iron (about 0.3 %) as well as a minor contribution of potassium. Trace elements show overall low concentration, usually below the detection limit, but there are some exceptions, such as barium, that varies between around 2-28 ppm, and strontium, that can reach levels around 180 ppm.

Table 2.3 The average, minimum, and maximum of the major elements in (weight percent) of the limestone and marl of the Slite Group (Shaikh et al., 1990).

	Elemental composition	Average Weight %	Max Weight %	Min Weight %
Limestone	CaO	53.14	55	49.5
	SiO_2	1.89	5.4	0.4
	Al_2O_3	0.73	1.32	0.29
	TiO_2	0.03	0.07	0*
	Fe_2O_3	0.36	0.72	0.17
	MnO	0.02	0.03	0.01
	MgO	0.70	1.22	0.18
	K_2O	0.20	0.48	0.04
	Na_2O	0.04	0.06	0.02
	S	0.02	0.12	0*
Marl	CaO	41.57	49.6	33.5
	SiO_2	13.00	20.7	5.7
	Al_2O_3	2.69	4.21	1.17
	TiO_2	0.15	0.24	0.05
	Fe_2O_3	1.13	1.42	0.68
	MnO	0.07	0.13	0.04
	MgO	2.87	4.93	0.19
	K_2O	0.89	1.51	0.38
	Na_2O	0.17	0.21	0.1
	S	0.14	0.21	0.04

Table 2.3 The average chemical data of two drill cores from Storugns quarry (Shaikh et al.,1990).

Storugn-Chemical data	**Weight %**	**Storugn-Chemical data**	**Weight %**
CaO	53.3	MnO	0.02
SiO_2	1.55	MgO	0.81
Al_2O_3	0.76	K_2O	0.21
TiO_2	0.03	Na_2O	0.30
Fe_2O_3	0.34	S	0.08

2.3 Principles of limestone analysis

Rock samples were acquired from mines, corporations, and colleagues. Peltola et al. (2015) prepared the thin sections. The mineralogy was studied under a petrographic microscope. The powders were prepared by crushing the stones with a jaw crusher and subsequently grinding to smaller particles with a vibratory disc mill. Using sieves, a suitable amount of material for dissolution and characterization experiments was gathered to three size fractions of 63 – 106 µm, 106 – 150 µm, and 150 – 250 µm. Each sample fraction was first rinsed 4 – 6 times with tap water (pH ~8.0) and finally twice with distilled water to remove fine particles. The resulting samples were dried under ambient laboratory conditions. Two of the most widely used classifications are those of Folk (1959, 1962) and Dunham (1962). Both classifications subdivide limestones primarily based on matrix content as shown in Figure 2.7 and Figure 2.8.

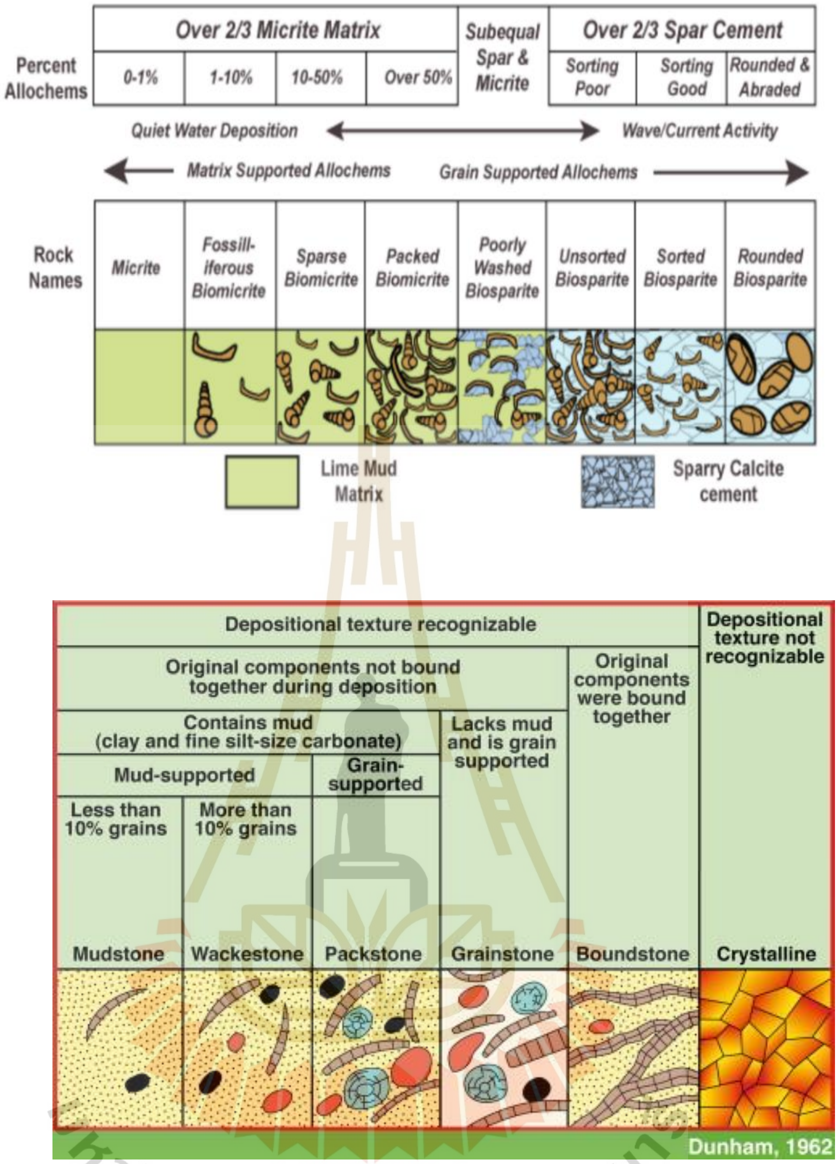


Figure 2.8 Dunham's textural classification of carbonate sediment.

Oyedotun (2015) described X-ray Fluorescence Spectrometry (XRF) is a non-destructive analytical technique was used to determine the major elemental composition of 21 sediment samples from the estuarine and coastal systems. The major elements in their oxidized state were determined as a percentage of the composition. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays ("a fingerprint") that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition.

Bragg (1913) described X-ray diffraction is a powerful characterization technique used in the analysis of crystalline solids that exhibit long-range order, i.e. when the atomic positions are repeated regularly. When impacted by light or radiation, a 3-dimensional array of atoms, molecules or ions, cause the light to be diffracted, as described by W. H. Bragg and W. L. Bragg in 1913. This behavior is summarized by the expression, $n\lambda = 2\ d\ \sin\Theta$ (Bragg's Law) where λ = wavelength of radiation used (in our case, Cu [Copper] radiation, λ = 1.5408Å), d = interplanar spacing within the crystalline solid and Θ represents the incident angle between the x-rays and sets of parallel "planes" in the crystalline solid. For diffraction to be observed (constructive interference), Bragg's law must be satisfied (Figure 2.6).

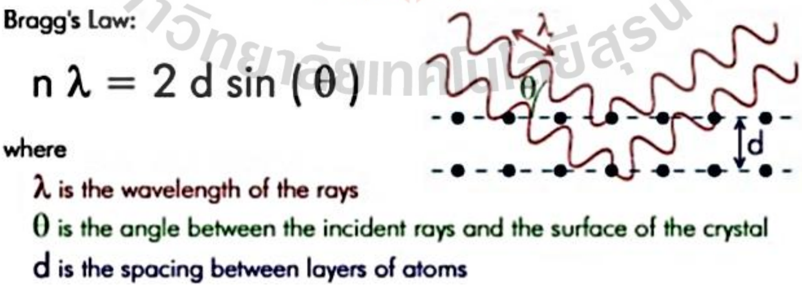


Figure 2.9 Bragg's law and equation**.**

Reimer (1998) discussed that the scanning electron microscopy (SEM) is a versatile technique used in many industrial labs, as well as for research and development. Due to its high lateral resolution, its great depth of focus, and its facility for X-ray microanalysis, SEM is often used in materials science-including polymer science to elucidate the microscopic structure or to differentiate several phases from each other. After a brief historic overview, this chapter explains the assembly and the mode of operation of SEM, which deviates from standard microscopes. This includes descriptions of the fundamentals of electron optics, the electron optical column, and the physical basics of electron-specimen interactions, which aid the understanding of contrast formation and charging effects. Because it is important to know the factors that influence X-ray microanalysis, a separate section about the origins of X-ray spectra and their interpretation has also been added. A discussion of environmental scanning electron microscopy (ESEM^{TM}) – a special development of SEM that is particularly useful when nonconducting or "wet" samples are to be examined completes the chapter.

2.4 Acidizing in carbonate and sandstone

McLeod (1894) presented guidelines for acid selection based on extensive field experience. His recommendations for sandstone reservoirs are shown in Table 2.5 These guidelines should not be taken as hard-and-fast rules, but rather as starting points in treatment design.

McLeod (1984) reported the hydrochloric acid is by far the most common acid used in carbonate matrix acidizing. Table 2.5 shows the acids suggested by McLeod (1984) for various acid treatments of carbonate formation. Weak acids are suggested for perforation cleanup and perforating fluid, but otherwise, strong solutions of HCl are recommended. For a matrix treatment, HCl should be used unless corrosion considerations required a weaker acid. All models of wormhole propagation predict deeper penetration for higher acid concentrations, so a high concentration of HCl is preferable. Also, in carbonates, there are no precipitation reactions to limit the acid concentrations used, as is the case in sandstones (Table 2.6).

Table 2.5 Acid selection guidelines for sandstone acidizing (McLeod, 1894).

Sandstone Acidizing	
HCl solubility > 20%	Use HCl only
High permeability (100 md plus)	
High quartz (80%), low clay (<5%)	10 % HCl - 3%HF
High feldspar (>20%)	13.5% HCl – 1.5 HF
High clay (>10%)	6.5% HCl – 1 HF
High iron chlorite clay	3% HCl – 0.5 HF
Low permeability (10 md or less)	
Low clay (<5%)	6% HCl – 1.5% HF
High chlorite	3% HCl – 0.5% HF
[a]Preflush with 15% HCl	
[b]Preflush with sequestered 5% HCl	
[c]Preflush with 7.5% HCl or 10% acetic acid.	
[d]Preflush with 5% acetic acid	

Table 2.6 Acid selection guidelines for carbonate acidizing (McLeod, 1894).

Acid Use Guidelines: Carbonate Acidizing
Perforating fluid:
5% acetic acid
Damaged perforations:
9% formic acid
10% acetic acid
15% HCl
Deep wellbore damage:
15% HCl
28% HCl
Emulsified HCl

University of Massachusetts Amherst (2011) showed the reaction of metal carbonates or bicarbonates with acids produces the metal halide and carbonic acid, which decomposes to carbon dioxide and water as equation (2.1), (2.2). and (2.3) :

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2CO_3(aq) \quad (2.1)$$

$$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g) \quad (2.2)$$

Overall: $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ (2.3)

The concentration of solutions can affect the rate of the reaction. In this case, the higher the concentration of the acid, the faster the reaction takes place.

Tantindai (2016) studied acidizing in the sandstone of Phra Wihan Formation. The experimental results indicated that the sample permeability can be changed using the Acidizing technique. This period affects directly on the sample permeability. The sample that was saluted for a longer time might create mineral precipitate, and results to reduce sample permeability. In the addition, the acid with high concentrate can improve the sample permeability better than acid with low concentrations in a similar condition, but the acid with concentrate must be appropriate based on composites mineral of sandstone sample. Postflush causes fine particle plugging a channel in the rock sample. The heterogeneity of mineral compositions of the sample was the most important issue for this study, this issue created a significant error to experimental results. Experimental of acidizing relative permeability results are shown in Table 2.7.

Table 2.7 Acidizing Relative Permeability (Ks/Ki) Tantindai (2016).

Sample No.	**HCl - HF Concentrate**	**Ks / Ki**					
		8 hr.	**16 hr.**	**24 hr.**	**32 hr.**	**40 hr.**	**48 hr.**
1	7.5 - 1.5%	1.0858	1.0963	1.1117	1.0963	1.1067	1.0018
2	7.5 - 1.5%	1.0159	0.9867	0.9956	0.9001	0.9496	0.9014
3	12 - 3%	1.2445	1.2262	1.2573	1.1919	1.3371	1.6195
4	12 - 3%	1.0135	0.8887	0.8133	0.8356	0.7874	0.6014

Almarri (2015) studied is to understand how different dissolution patterns which form during a typical acid treatment affect the overall effectiveness of an acidizing treatment. Several factors that affect the dissolution pattern were investigated; injection rate, acid concentration, permeability- porosity relations, heterogeneity magnitude, reservoir pressure, reaction rate, mineral solubility, and acid diffusivity. Each of these factors has a different magnitude of influence on the resulting dissolution pattern. Lastly, the results of our base case simulation run were scaled up to field conditions. Below are several take-away points from the study:

- Contrary to field practices, the optimum acid injection rate is not the highest possible injection rate without fracturing the formation.
- The injection rate is the most critical parameter for creating a well conductive wormhole. Also, it's the single parameter that can be easily altered during a stimulation job. Therefore, extra precautions need to be put in place to maintain an accurate injection rate.
- Field engineers need to understand the physics of the dissolution caused by pumping acid treatments.
- The higher the reservoir pressure the lower the amount of acid needed for breakthrough.

Shuchart et al. (1996) reported two field treatments using acetic-HF and formic-HF. In both treatments, there was significant precipitation of aluminum fluoride, particularly in the acetic-HF system. The study of the interaction of organic-HF systems with the formation of minerals and the potential precipitation, batch reactions with only kaolinite at 75^{o}F and 200^{o}F were conducted. The following acids were evaluated in this set of experiments: 10%formic-1%HF, 10%formic 1.5%HF, 10%acetic-1%HF, 10%acetic-1.5%HF, and two new systems based on organic acid. Also, column packed tests (90% sand& 10% bentonite) was performed to compare the performance of 10%acetic-1%HF with a new system based on organic acid. The permeability increased from 20 mD to 25 mD when the column was treated with acetic-HF. In the other system, the overall permeability increased from 20 mD to 35 mD. While formic-HF treatment failed to give sustained production increases, the new system treatment in the same well resulted in three-fold production increase that lasted for more than 4 months.

SPE, Petroleum Engineering Handbook (1987) explained that the concentration of solutions can have an effect of the rate of the reaction. In this case, the higher the concentration of the acid, the faster the reaction takes place but this is not always the case, because the higher the acid concentration, the faster the reaction accelerates, resulting in filling pore and coating the contact surface makes the matrix less dissolving according to figure 2.10. as showed effect of acid concentration on reaction rate and spending time. The selection of the acid concentration requires consideration of its suitability for use and economics. In addition, the selection of acidic concentrations at high concentrations can also contribute to corrosion of production equipment and environmental problems.

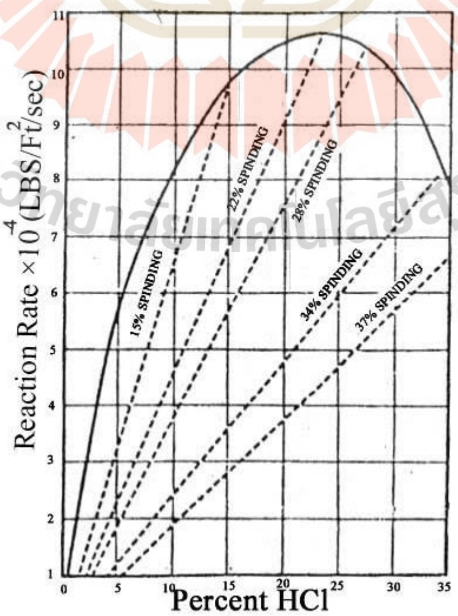


Figure 2.10 Effect of acid concentration on reaction rate and spending time

CHAPTER III

RESEARCH METHODOLOGY

This research presents a test for limestone dissolution by using hydrochloric acid. Physical properties test of limestone with lab equipment such as Scanning Electron Microscope (SEM), Porosimeter, Microscope. Testing chemical properties with lab equipment such as X-ray Powder Diffraction (XRD), and X-ray Fluorescence (XRF).

3.1 Sample collections

The sampling area is in the northeastern region of Thailand by collecting three formations in Loei and Nakhon Ratchasima provinces as follows.

3.1.1 Nam Mahoran Formation

Figure 3.1 shows the sampling area of Nam Mahoran Formation is collected from the area of Erawan district, Loei province in the coordinates 1904041 N813385E.

Figure 3.1 Outcrop of Nam Mahoran Formation

3.1.2 Pha Nok Khao Formation

Figure 3.2 shows the sampling area of Pha Nok Khao Formation is collected from Phu Kradueng District, Loei Province in the coordinates 1866432 N814313E.

Figure 3.2 Outcrop of Pha Nok Khao Formation.

3.1.3 Khao Khad Formation

Figure 3.3 shows the sampling area of Khao Khad Formation is collected from Pak Chong district. Nakhon Ratchasima province in the coordinates 1613738N752478E.

Figure 3.3 Outcrop of Khao Khad Formation.

3.2 Sample Preparations.

Sample preparation is a procedure that is making a sample rock set to cut / drill/hammer to get the right shape for testing in various tools.

3.2.1 Core Sample Preparation

The purpose of the drilling of core samples is to bring the core sample into the Porosimeter tool to determine the porosity in the limestone. The drilling pattern and drilling tools are shown in Figure 3.4 and after drilling is complete, the characteristics of core samples are shown in Figure 3.5.

Figure 3.4 Core sample drilling process.

Figure 3.5 Core sample (Diameter = 37 mm in and High = 58 mm).

3.2.2 Thin section

The process of making a transparent sheet is attaching the stone to glass and scrub it and then look into the microscope to see the texture, minerals, and other elements of the limestone. The device for making a thin section is shown in Figure 3.6. and cutting machines and polishing tools are shown in Figure 3.7.

Figure 3.6 Equipment and composition for making a thin section (A) Glass, (B) Limestone the same size as glass, (C) Epoxy glue (D) Grit SiC Powder.

Figure 3.7 Cutting machines and polishing tools for making thin section.

3.2.3 Powder for XRD and XRF.

This step is the process of the stone to grind it into powder by ball mill machine as shown in Figure 3.8 for X-ray powder diffraction (XRD) test, and XRF (X-ray fluorescence) test in the next process.

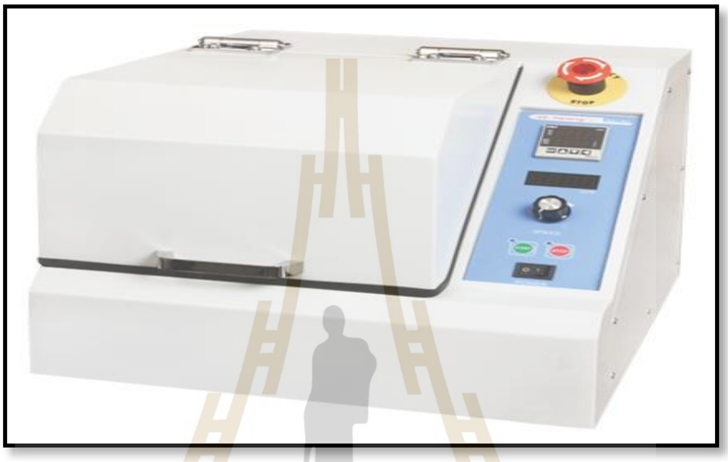


Figure 3.8 Ball Mill Machine model BRS-series.

3.2.4 Small pieces for SEM.

This step is the process of making the limestone into a small piece as shown in Figure 3.9 for the watching microstructure by Scanning Electron Microscope (SEM).

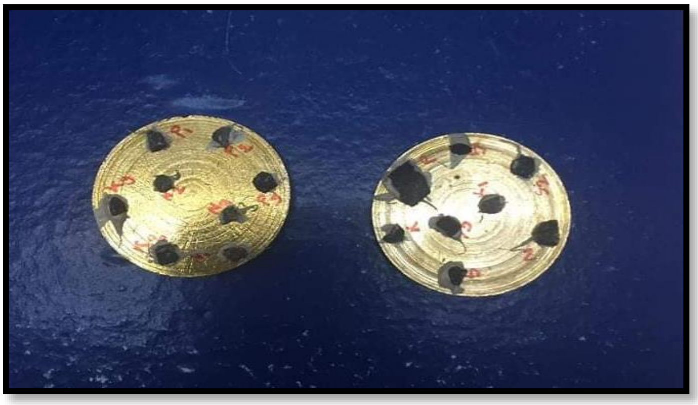


Figure 3.9 A small piece of sample for the Scanning Electron Microscope (SEM).

3.3 Dissolution with hydrochloric acid (HCl)

The samples are soaked with 12M of HCl with a concentration of 5%, 10%, 15%, and 20% of HCl for 24 hours as showing in Figure 3.10. This experiment was tested at room temperature under ambient condition and washed with water before porosity, SEM, XRD, and XRF analysis.

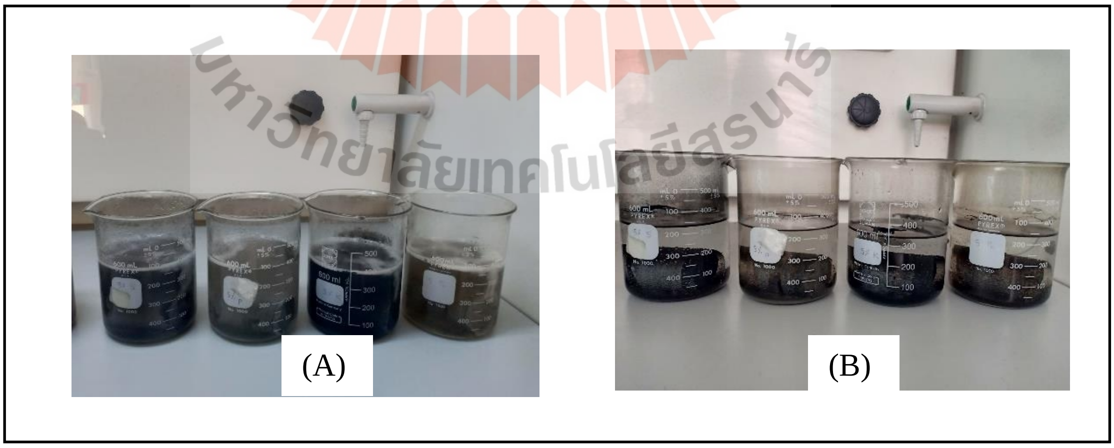


Figure 3.10 Limestone dissolution with hydrochloric acid. (A) Limestone while soaking (B) Limestone after soaking.

3.4 Chemical analysis

Chemical analysis is considered one of the methods of sample analysis by using crushed samples to test for the mineral composition and chemical elements of the sample rock set.

3.4.1 XRF (X-ray fluorescence)

An X-ray Fluorescence (XRF) analyzer is a proven scientific instrument for analyzing the chemical properties of the material in a broad range of industries and applications. It works by exposing samples to be measured to be a beam of primary X-rays. Each chemical element emits X-rays at unique energy by measuring the intensity and characteristic energy of the emitted X-Rays, and XRF analyzer can provide qualitative and quantitative analysis regarding the thickness and composition of the material being tested

XRF analysis is a chemical element analysis that is done by grinding the samples into the XGT-5200 X-Ray analytical microscope and translation through the computer as shown in Figure 3.11. The result will be a graph showing the percentage concentration of chemical elements according to the periodic table as shown in figure 3.10. and save the data in PDF format.

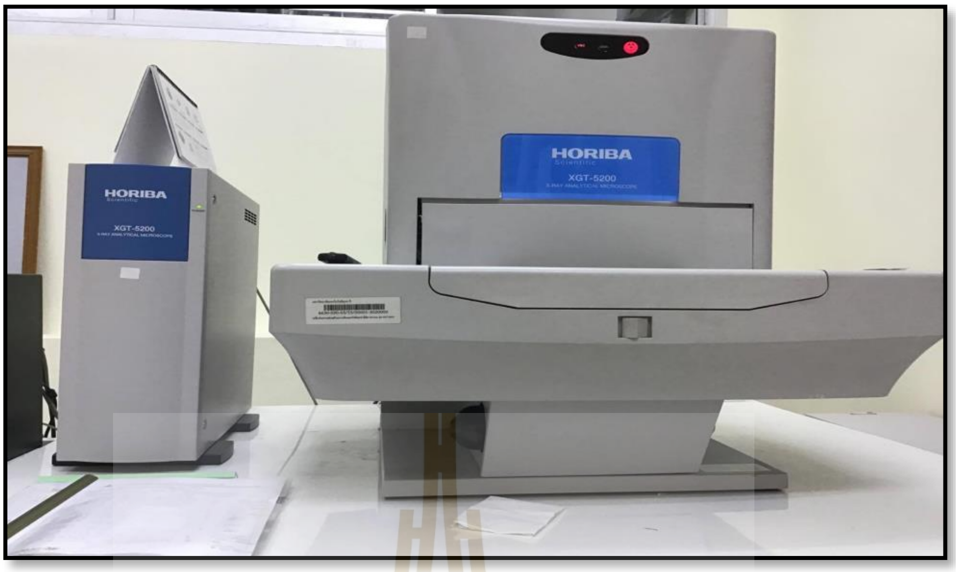


Figure 3.11 XGT-5200 X-Ray analytical microscope.

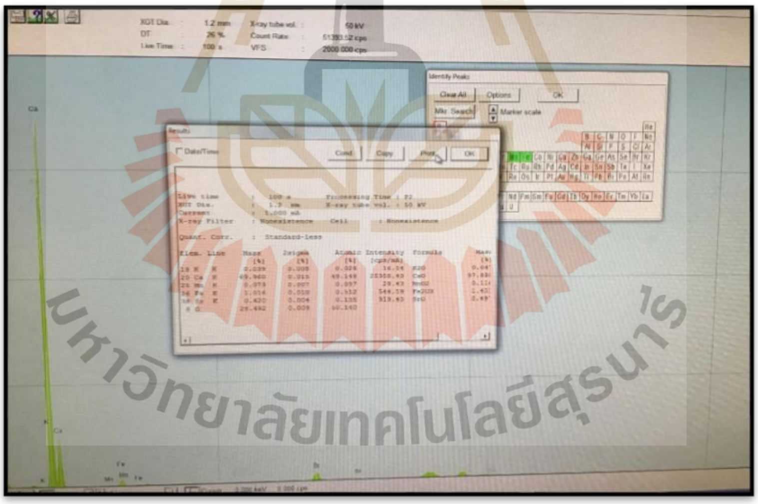


Figure 3.12 Sample screen while showing XRF translation results.

3.4.2 X-ray diffraction (XRD)

X-Ray Diffraction (XRD) analyses were done on the powder samples in XRD-D2 and translate data by the computer as shown in Figure 3.14 and 3.14 which were compacted in a Cu X-ray tube. The XRD traces were obtained by scanning at 0.1º(2θ) per min and steps of 0.05º(2θ). The result will be a graph showing the presence of minerals in the form of mineral compositions that are combined with oxygen and the graph has to be interpreted peak in 2theta which computers do not interpret save the data in PDF format. Finally, save the data in PDF format.

Figure 3.13 XRD-D2 Phaser analysis.

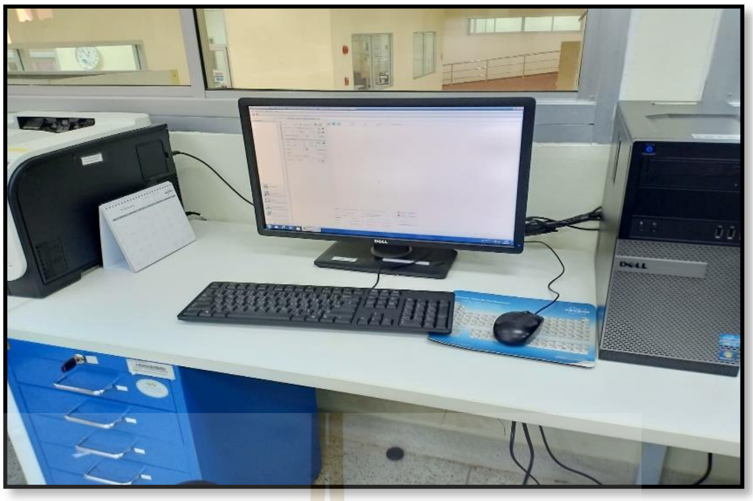


Figure 3.14 Sample screen while showing XRD translation results.

3.5 Porosimeter test

Porosimeter tool (as shown in Figure 3.15) is one of the methods used to find pore in the rock by compressing the gas through the Porosimeter and using the gas replacement method to replace the pores in the rock. Sample preparation for Porosimeter testing is done by making a core sample (Diameter 3.75 cm in length, about 6 cm in length). The test method will find the reference volume and gain volume by reading from the instrument and calculate the bulk volume and porosity respectively.

The procedure for using porosimeter is as follows (according to Asst. prof. Kriangkrai Trisarn's Rock & Fluid properties Lab book).

a) Connect Helium gas supply to the port at the rear of the instrument as shown in figure 3.16

b) Calibrated and equipment leak checked on set up and checked periodically after that.

c) Determine the Reference Volume of the reference chamber (RV)

1. Fill the matrix cup with billets and seal the cup in the porosimeter such as shown in figure 3.17
2. Fill the reference chamber with helium to 100.00 psig. Record pressure as **Pof.** in Porosity-Lab sheet as shown in figure 3.18
3. Open the reference chamber to the sample chamber. Record the equilibrated pressure as **Pf.**
4. Remove the appropriate billet from the chamber. The volume of the billet removed should be approximately equal to the pore volume of the samples being tested. Record the volume of the billet removed as $\mathbf{V_{bill}}^{1}$ (cm^3)
5. Repeat steps 2 and 3, this time record the reference chamber pressure as **Pob** and the equilibrated pressure of the sample chamber as **Pb**.

d) Place the clean and dried core sample in the matrix cup. If the sample is short, then fill the excess space with a billet(s). Record the identification number of the billets left out of the cup. The volume of these billets ($\mathbf{V_{bill}^{2}}$).

e) Fill the reference chamber with helium to 100.00 psig. Record the pressure as **Pos.**

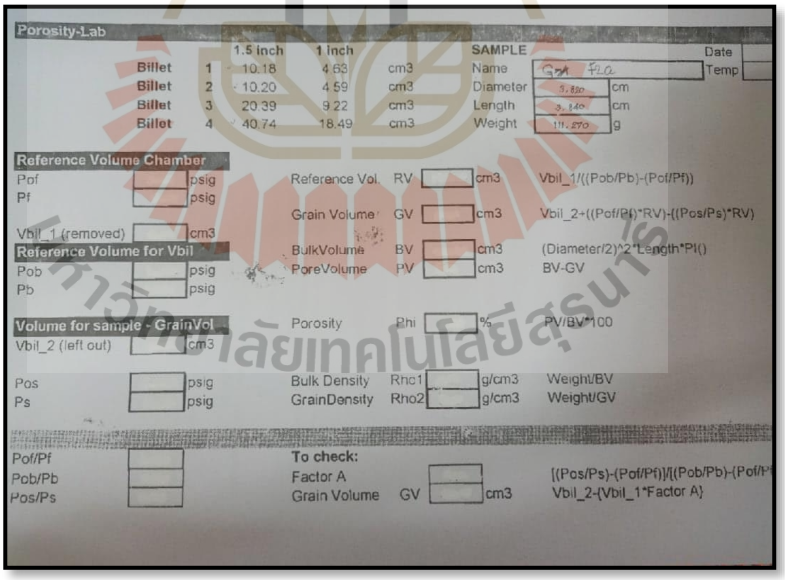
f) Introduce the helium into the matrix cup and allow the pressure to stabilize. Record the stabilized pressure as **Ps**.

g) Take all the obtained results above to calculate Gain Volume (**GV**).

Figure 3.15 Porosimeter tool.

Figure 3.16 Helium gas cylinder.

Figure 3.17 Matrix cup and billets.



Porosity-Lab

		1.5 inch	1 inch	
Billet	1	10.18	4.63	cm3
Billet	2	10.20	4.59	cm3
Billet	3	20.39	9.22	cm3
Billet	4	40.74	18.49	cm3

SAMPLE

Name

Diameter 3.820 cm

Length 3.840 cm

Weight 111.270 g

Date

Temp

Reference Volume Chamber

Pof psig

Pf psig

Vbil_1 (removed) cm3

Reference Volume for Vbil

Pob psig

Pb psig

Volume for sample - GrainVol

Vbil_2 (left out) cm3

Pos psig

Ps psig

Reference Vol.	RV	cm3	Vbil_1/((Pob/Pb)-(Pof/Pf))
Grain Volume	GV	cm3	Vbil_2+((Pof/Pf)*RV)-((Pos/Ps)*RV)
BulkVolume	BV	cm3	(Diameter/2)^2*Length*PI()
PoreVolume	PV	cm3	BV-GV
Porosity	Phi	%	PV/BV*100
Bulk Density	Rho1	g/cm3	Weight/BV
GrainDensity	Rho2	g/cm3	Weight/GV

Pof/Pf

Pob/Pb

Pos/Ps

To check:

Factor A [(Pos/Ps)-(Pof/Pf)]/[(Pob/Pb)-(Pof/P

Grain Volume GV cm3 Vbil_2-{Vbil_1*Factor A}

Figure 3.18 Porosity-Lab data sheet.

3.6 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is a method used to sample specimens prepared using a high-resolution microscope as shown in Figure 3.19 to see the pore of the rock before and after soaking the acid. The resolution can be adjusted to 5, 10, and 20 µm and can be adjusted visibility before saving the file.

Figure 3.19 JEOL JSM-6010LV Scanning Electron Microscope.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Introduction

This chapter describes the analysis of data and laboratory results, physical and chemical properties of limestone, both before and after soaking with hydrochloric acid at various concentrations. The test results and analysis are shown below:

4.2 Chemical properties

The objective of this test is to determine the composition and minerals of limestone, both before and after soaking with hydrochloric acid to analyze changes in chemical properties. These results lead to the determination of the optimal hydrochloric acid concentration to be used with limestone that is representative of the Permian limestone series in northeastern Thailand.

4.2.1 Chemical properties before soaking with hydrochloric acid

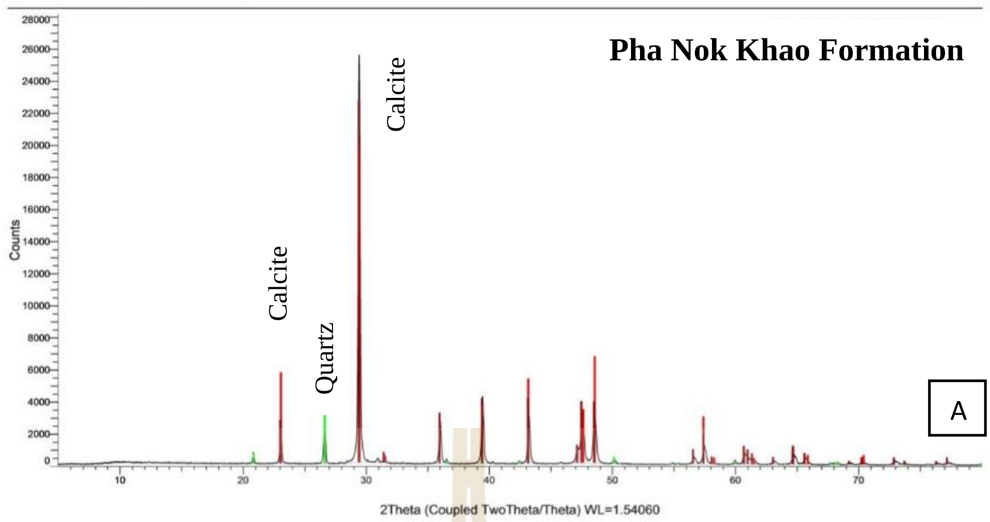
In the process of determining the chemical properties before soaking with hydraulic acid of Pha Nok Khao, Khao Khad, and Nam Mahoran Formation.

1) **Mineral composition**

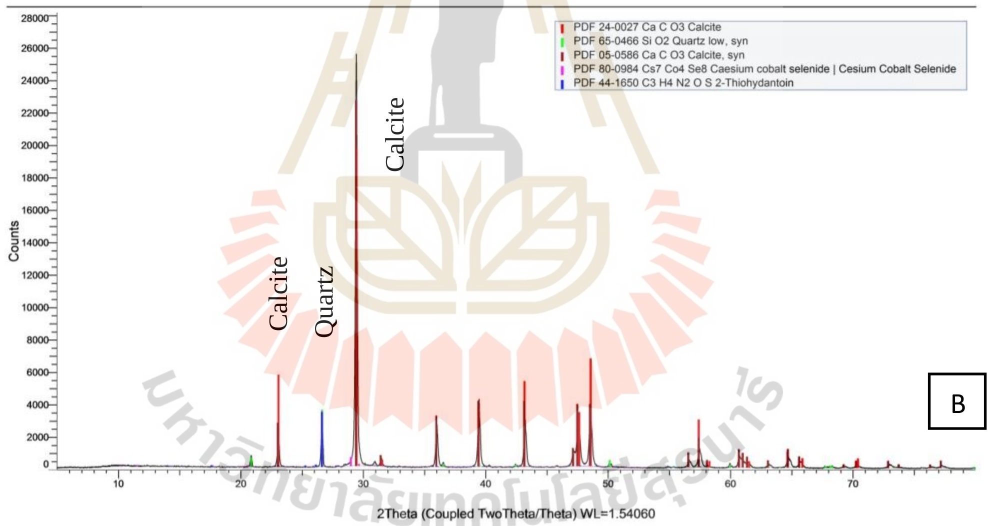
The mineral composition was analyzed by X-ray diffraction (XRD). From Figure 4.1 mainly showed the calcite that found in all three formations. The Khao Khad and Pha Nok Khao Formation have some quartz.

2) Elemental composition

Elemental composition was analyzed by X-ray fluorescence (XRF). Figure 4.2 showed the result of the elemental composition of each formation. The Pha Nok Khao Formation mainly consists of CaO as 96.29% with respectively minor of SiO_2, Fe_2O_3, Al_2O_3, SrO, K_2O, and TiO_2. The result of Khao Khad Formation highly consists of CaO as 98.83% with respectively minor of Al_2O_3, Fe_2O_3, SrO, K_2O, and TiO_2. The mainly elemental composition of Nam Mahoran Formation highly consists of CaO as 98.94% with respectively minor of SrO and Fe_2O_3.



Khao Khad Formation



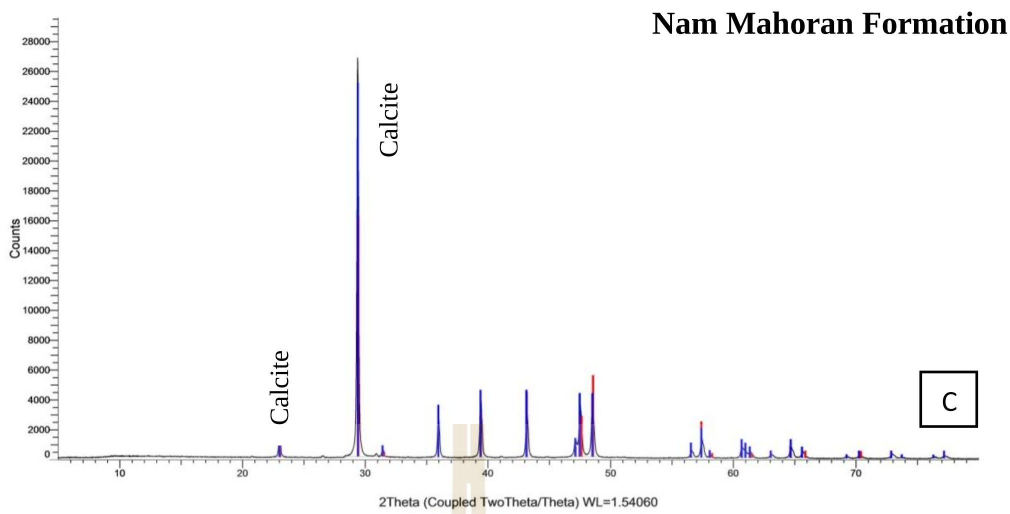
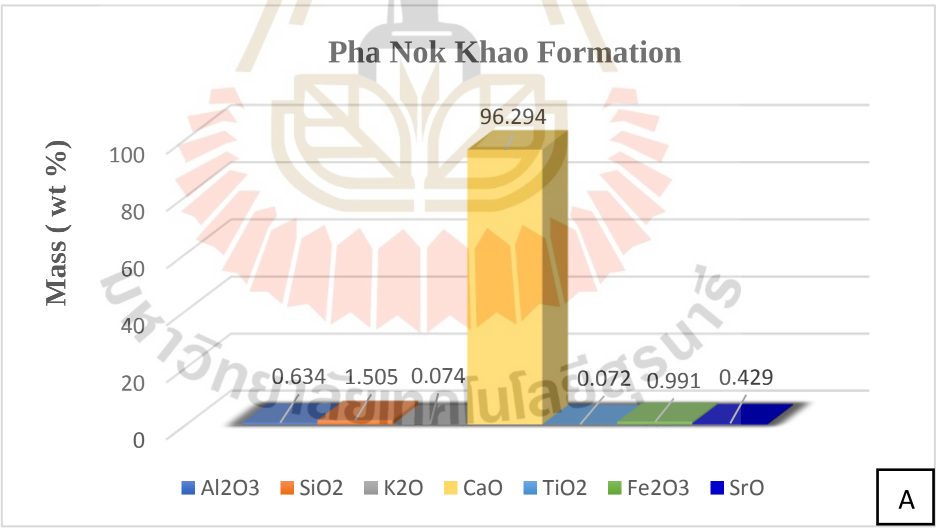


Figure 4.1 Mineral composition of each formation (A) Pha Nok Khao, (B) Khao Khad, and (B) Nam Mahoran Formation.



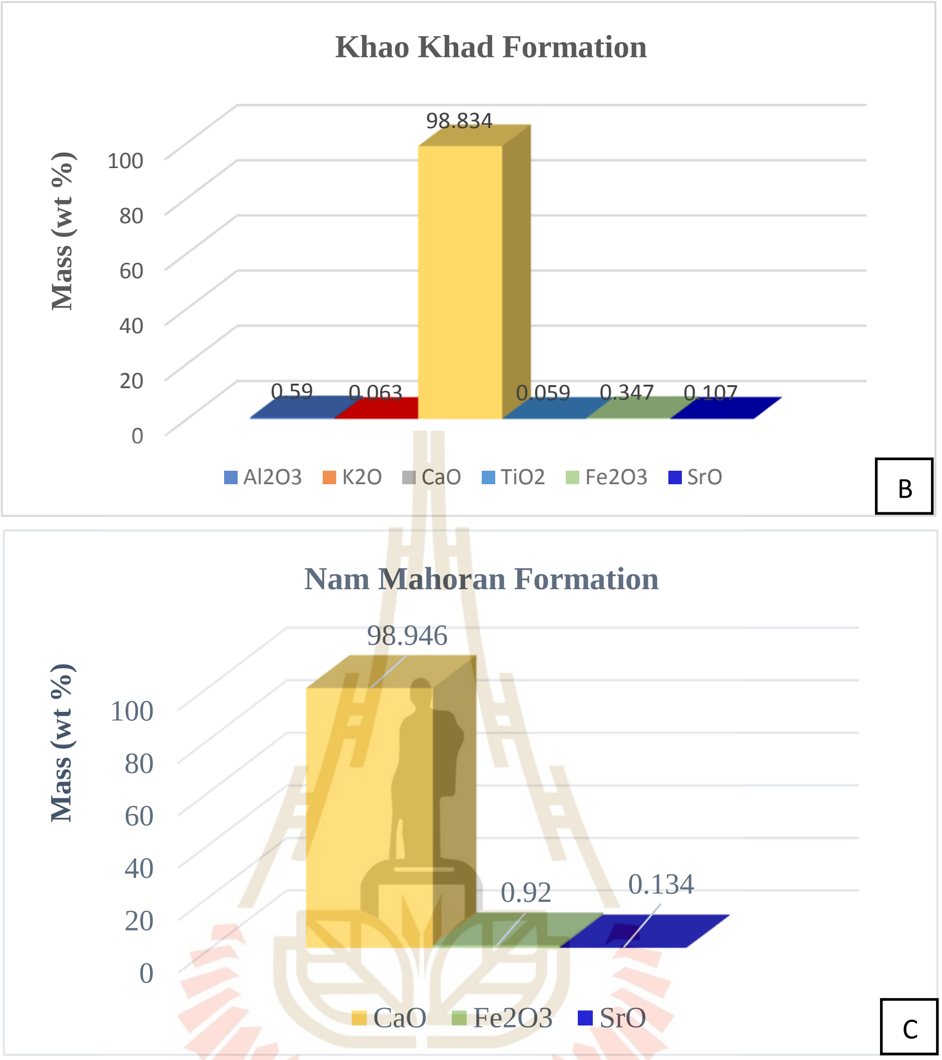


Figure 4.2 Oxide element compounds of each formation (A) Pha Nok Khao, (B) Khao Khad, and (B) Nam Mahoran Formation.

4.2.2 Chemical properties after soaking with hydrochloric acid

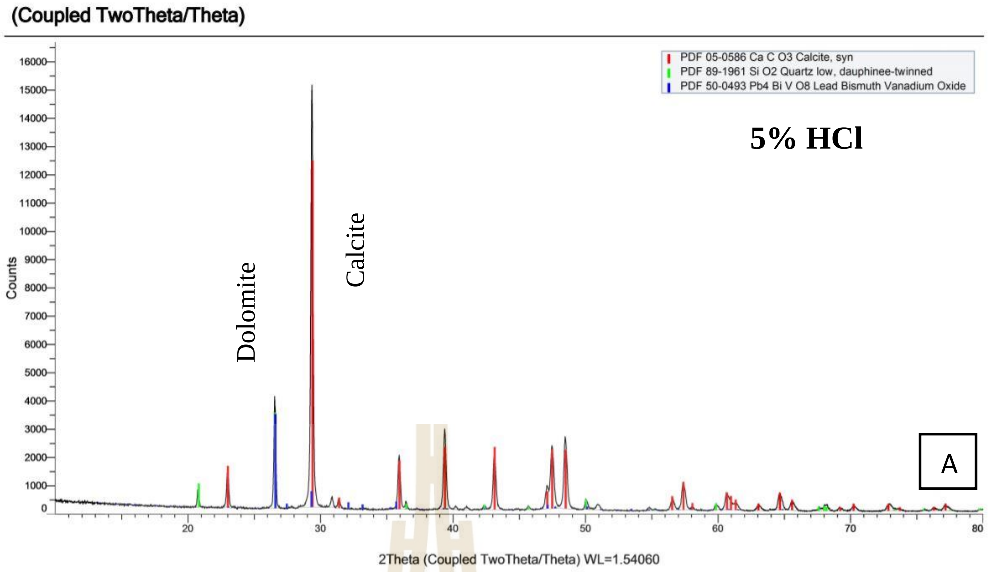
The process of determining chemical properties after soaking 5, 10, and 15% of hydrochloric acid (HCl). All of the three formations were done the same as before soaking the acid with the results as shown below:

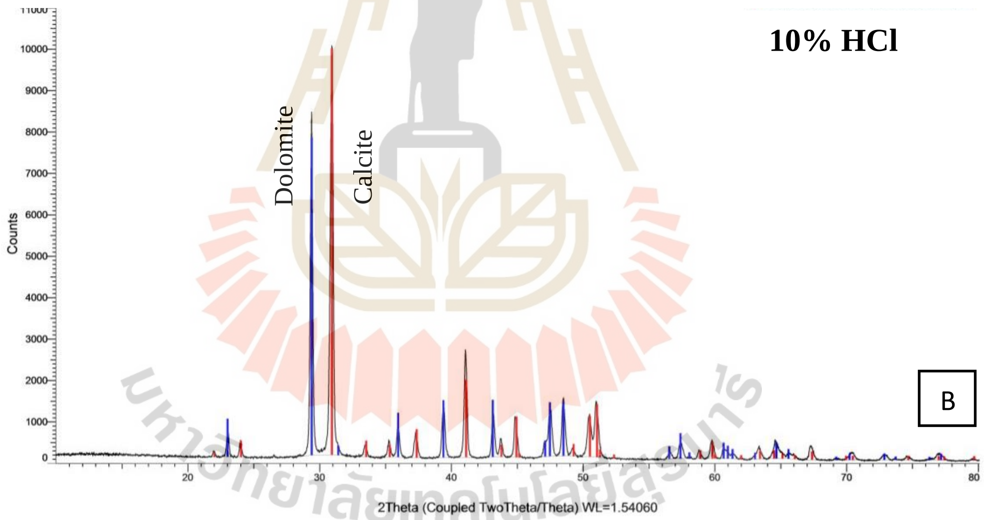
The result of XRD in Pha Nok Khao Formation after soaking with HCl acid found quartz and calcite for 5% HCl concentrate. The dolomite and calcite were found for the concentration of 10% and 15%. with HCl as shown in Figure 4.3.

The result of XRD in Khao Khad Formation after soaking with HCl acid found calcite and quartz minerals in all 5% with HCl concentrations. At 10% and 15% with HCl found the calcite mineral only as shown in Figure 4.4.

The result of XRD in Nam Mahoran Formation after soaking with HCl acid found the calcite mineral only in all concentrations (5%, 10%, and 15% HCl) as shown in Figure 4.5.

The chemical property of Permian limestone found that the calcite and CaO content in the Nam Mahoran Formation is greater than Khao Khad and Pha Nok Khao Formation, respectively. These content of calcite and CaO relate to the porosity and rate of matrix dissolution. The Pha Nok Khao Formation consists of the quartz and SiO_2 content resulting in the reduction of matrix dissolution.


(Coupled TwoTheta/Theta)
PDF 05-0586 Ca C O3 Calcite, syn
PDF 89-1961 Si O2 Quartz low, dauphinee-twinned
PDF 50-0493 Pb4 Bi V O8 Lead Bismuth Vanadium Oxide
5% HCl
Dolomite
Calcite
Counts
A
2Theta (Coupled TwoTheta/Theta) WL=1.54060


10% HCl
Dolomite
Calcite
Counts
B
2Theta (Coupled TwoTheta/Theta) WL=1.54060

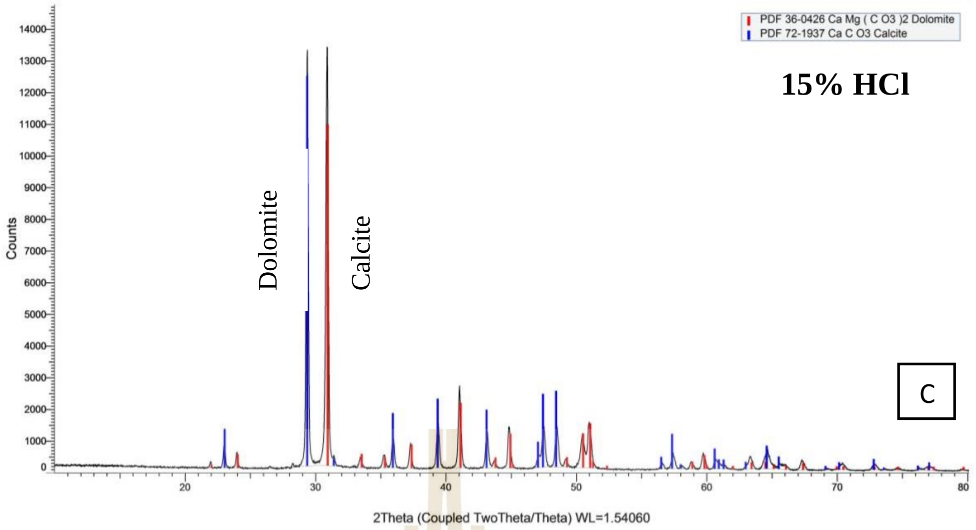
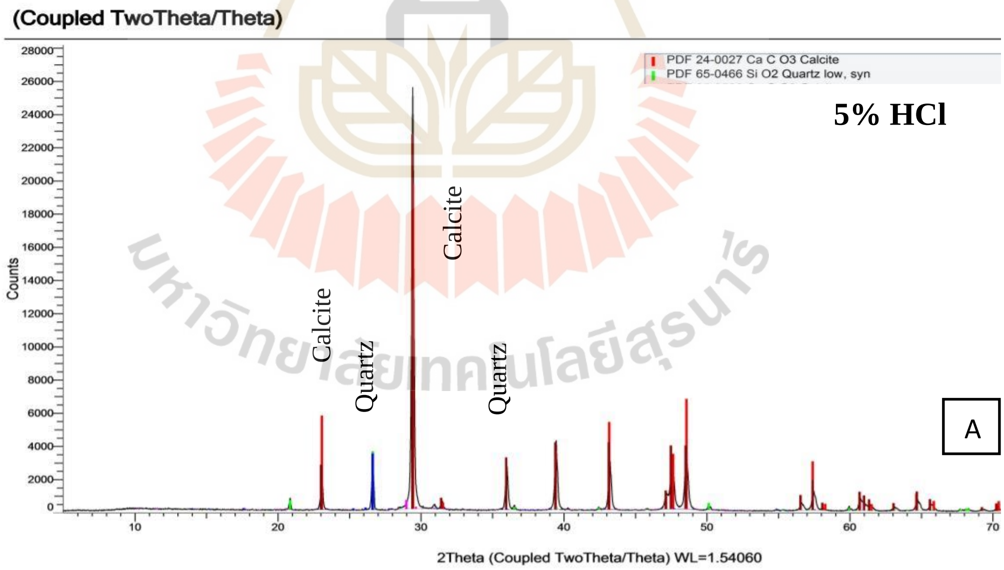


Figure 4.3 Mineral composition of Pha Nok Khao Formation after soaking with (A) 5% HCl, (B) 10% HCl, and (C) 15% HCl.



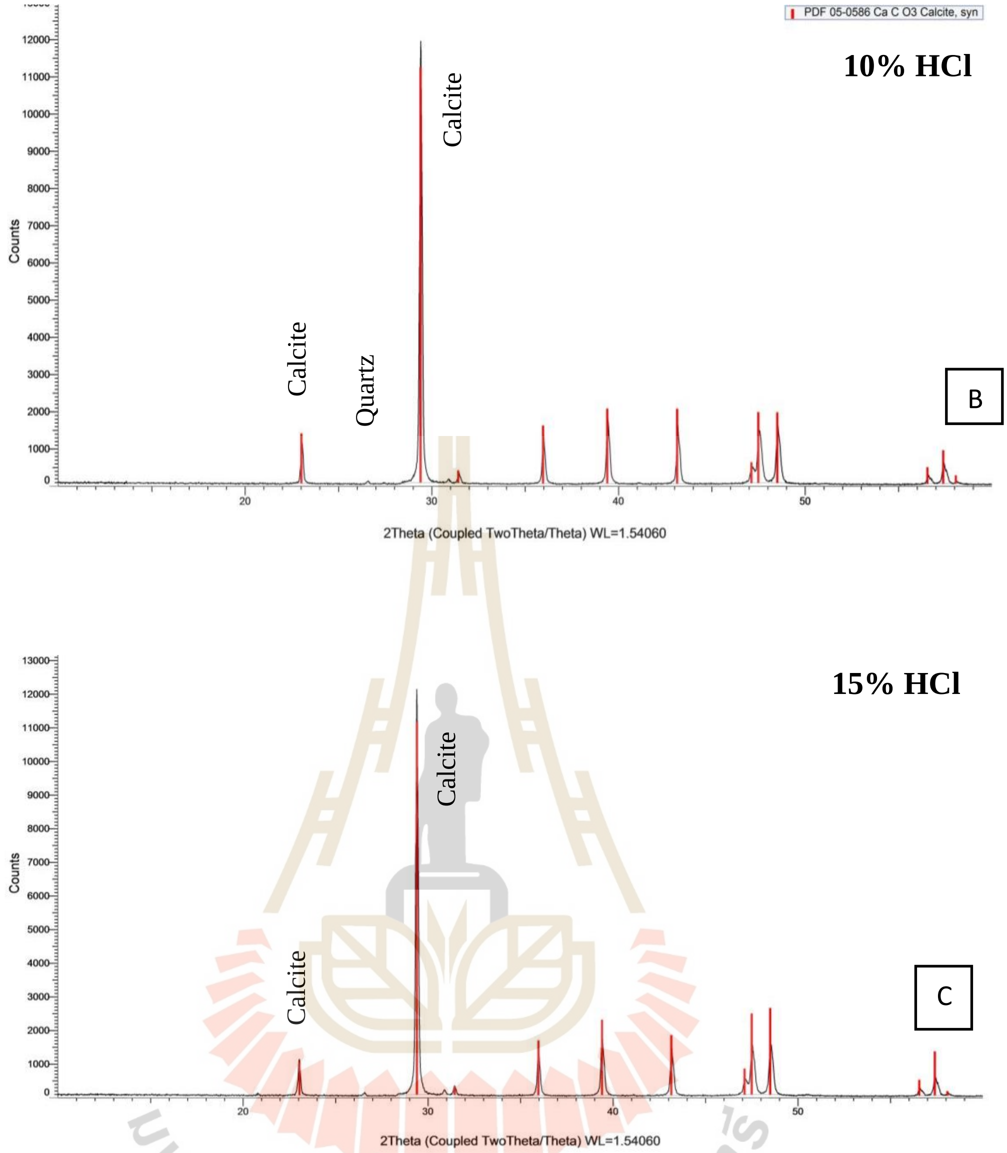
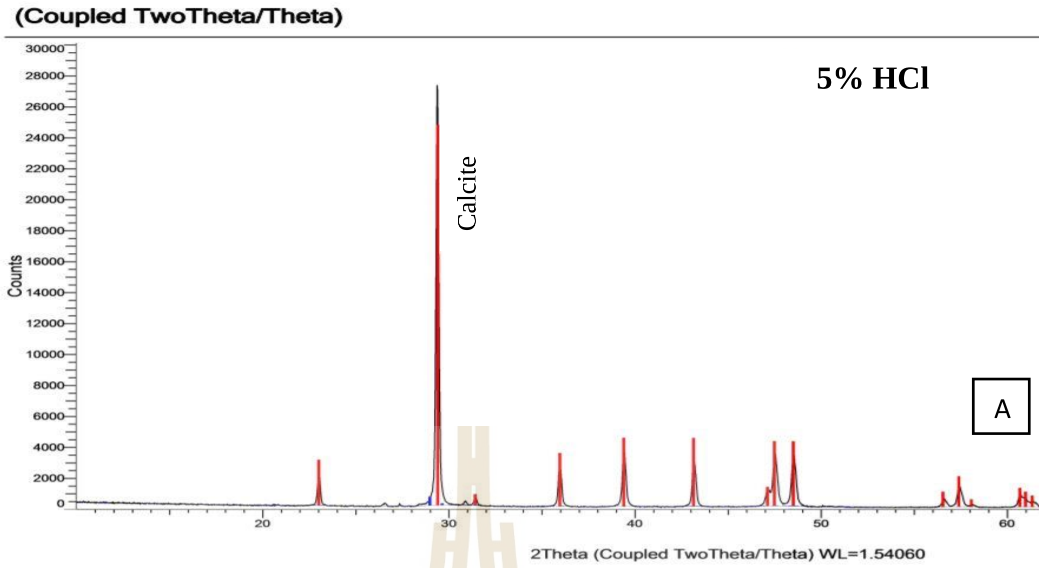
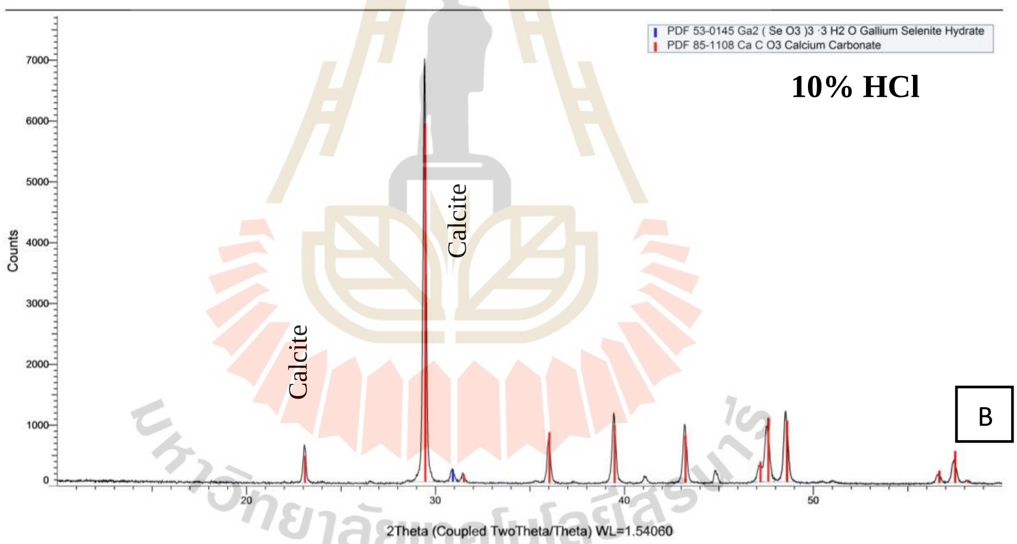


Figure 4.4 Mineral composition of Khao Khad Formation after soaking with (A) 5% HCl, (B) 10% HCl, and (C) 15% HCl acid.



(Coupled TwoTheta/Theta)
5% HCl
Calcite
Counts
2Theta (Coupled TwoTheta/Theta) WL=1.54060
A



PDF 53-0145 Ga2 (Se O3)3 ·3 H2 O Gallium Selenite Hydrate
PDF 85-1108 Ca C O3 Calcium Carbonate
10% HCl
Calcite
Calcite
Counts
2Theta (Coupled TwoTheta/Theta) WL=1.54060
B

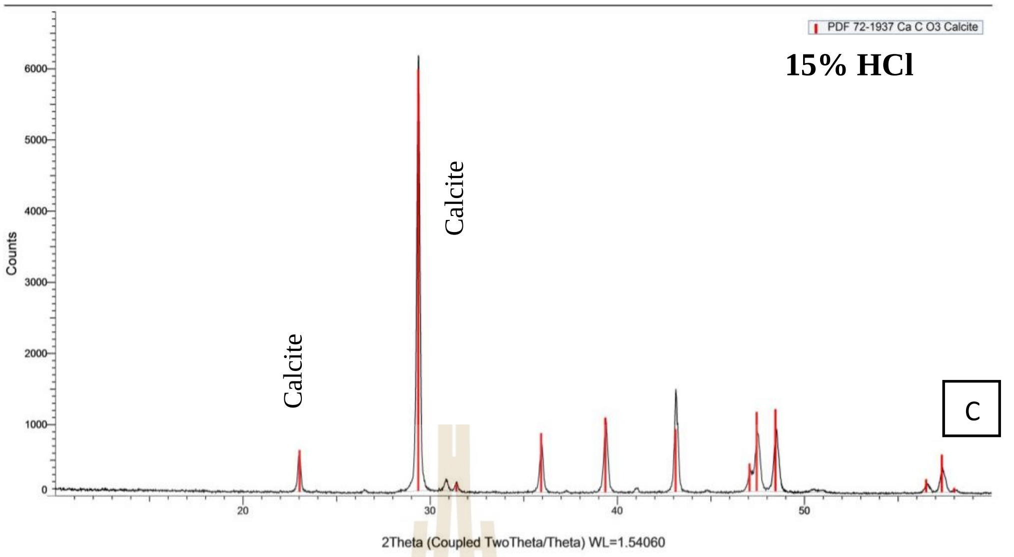


Figure 4.5 Mineral composition of Nam Mahoran Formation after soaking with (A) 5% HCl, (B) 10% HCl, and (C) 15% HCl acid.

Figure 4.6 showed the elemental result of the Pha Nok Khao Formation after soaking with HCl. The result of Pha Nok Khao Formation after soaking with 5% HCl mainly consists of CaO as 99.23% and respectively minor of Fe_2O, SiO_2, SrO, K_2O, and MnO_2. The result with 10% HCl concentration mainly consists of CaO as 96.80% and respectively minor of Fe_2O_3, MnO_2, SrO, and K_2O. The result with 15% HCl concentration mainly consists of CaO as 97.89%, and respectively minor of Fe_2O_3, MnO_2, SrO, and K_2O.

Figure 4.7 showed the elemental result of Khao Khad Formation after soaking with HCl. The result of Khao Khad Formation after soaking with 5% HCl mainly consists of CaO as 99.02%, and respectively minor of Fe_2O_3, SrO, and Al_2O_3. The result with 10% HCl concentration mainly consists of CaO as 99.47%, and respectively minor of Fe_2O_3, SrO, and K_2O. The result with 15% HCl concentration consists of CaO as 99.56%, and respectively minor of Fe_2O_3, SrO, and SO_3.

Figure 4.8 showed the results of XRF in Nam Mahoran Formation after soaking with HCl. The result of Nam Mahoran Formation after soaking with 5% HCl consists of CaO as 99.51%, and respectively minor of Fe_2O_3 and SrO. The result with 10% HCl concentration consists of CaO as 99.68%, and respectively minor of SrO and Fe_2O_3. The result with 15% HCl concentration consists of CaO as 99.74%, and respectively minor of SrO and Fe_2O_3.

After dissolving with 5%, 10%, and 15% of HCl in all formation, the content of calcite and CaO increases more than the original formation causing the matrix dissolution.

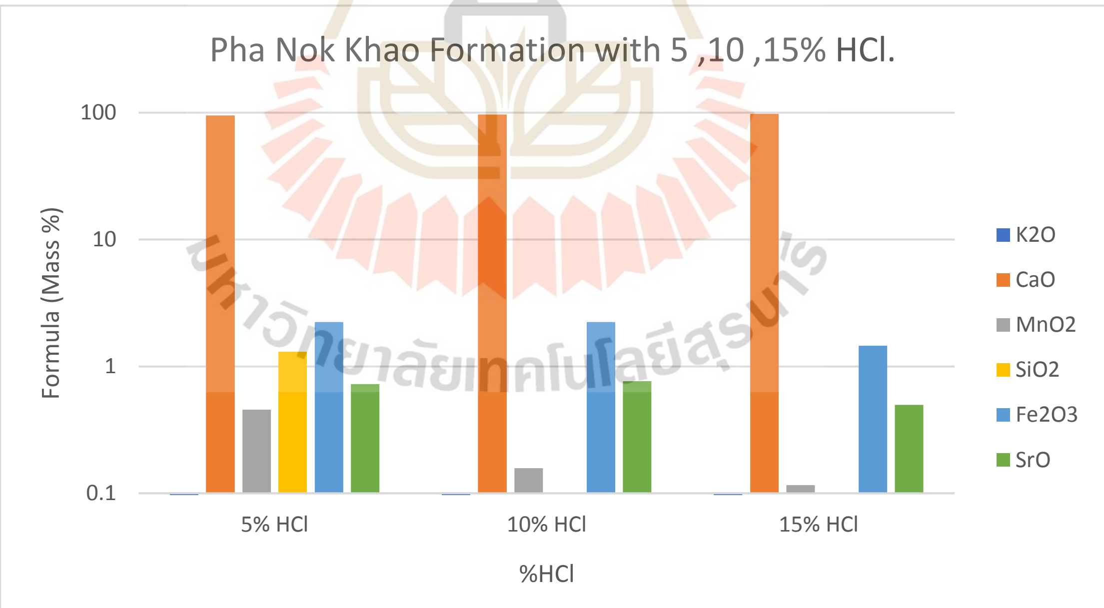


Figure 4.6 Oxide element compounds of Pha Nok Khao Formation after soaking with various concentrations of HCl acid.

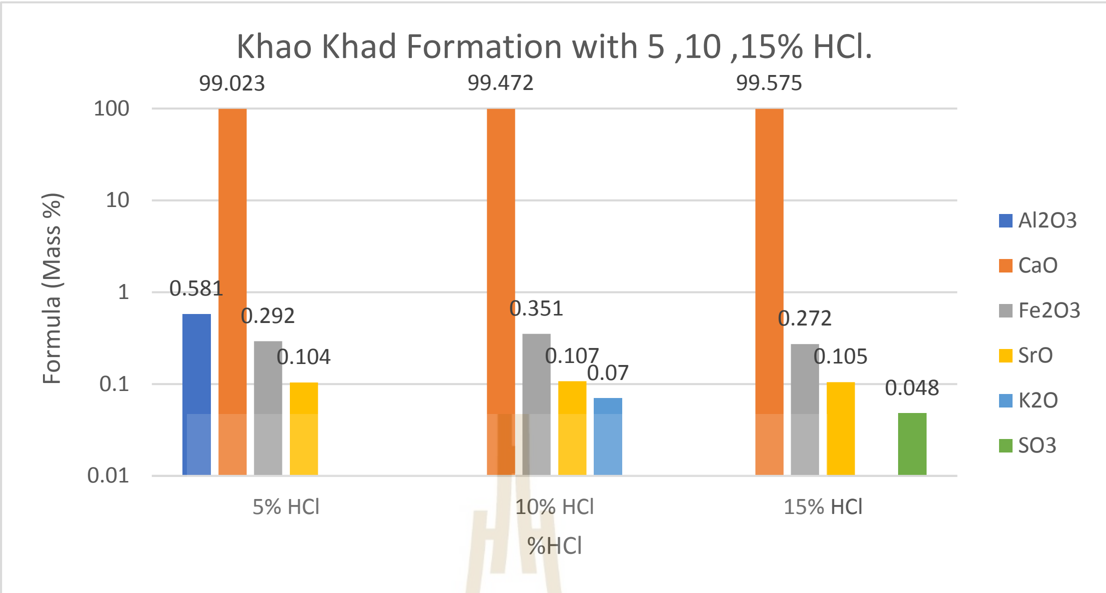


Figure 4.7 Oxide element compounds of Khao Khad Formation after soaking with various concentrations of HCl acid.

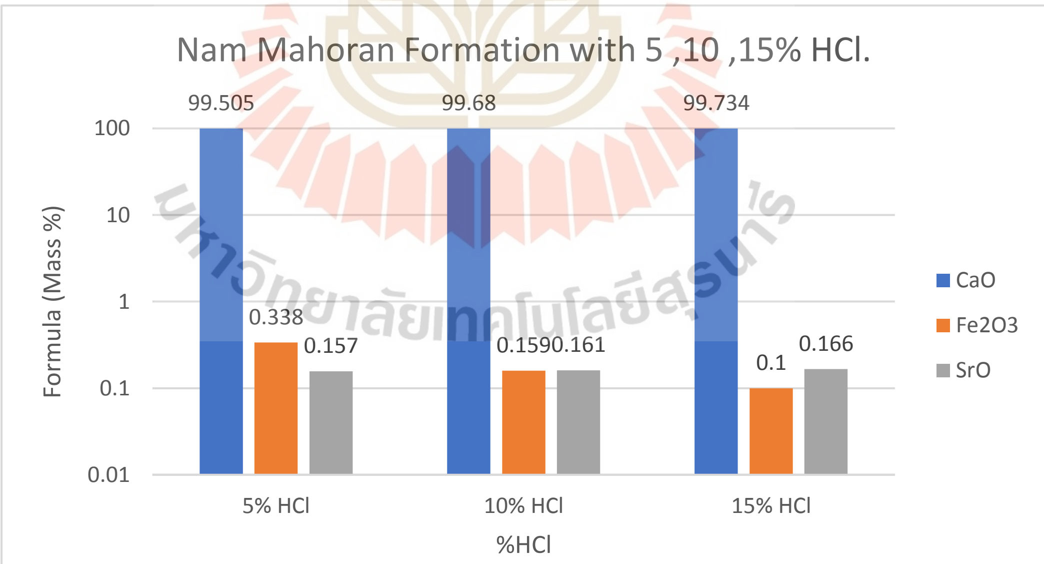


Figure 4.8 Oxide element compounds of Nam Mahoran Formation after soaking with various concentrations of HCl acid.

4.3 Physical properties

The objective of this test is to see the mineral rock composition observing the structure and internal pore of limestone including the effect of porosity in the texture both before and after soaking with hydrochloric acid at various concentrations.

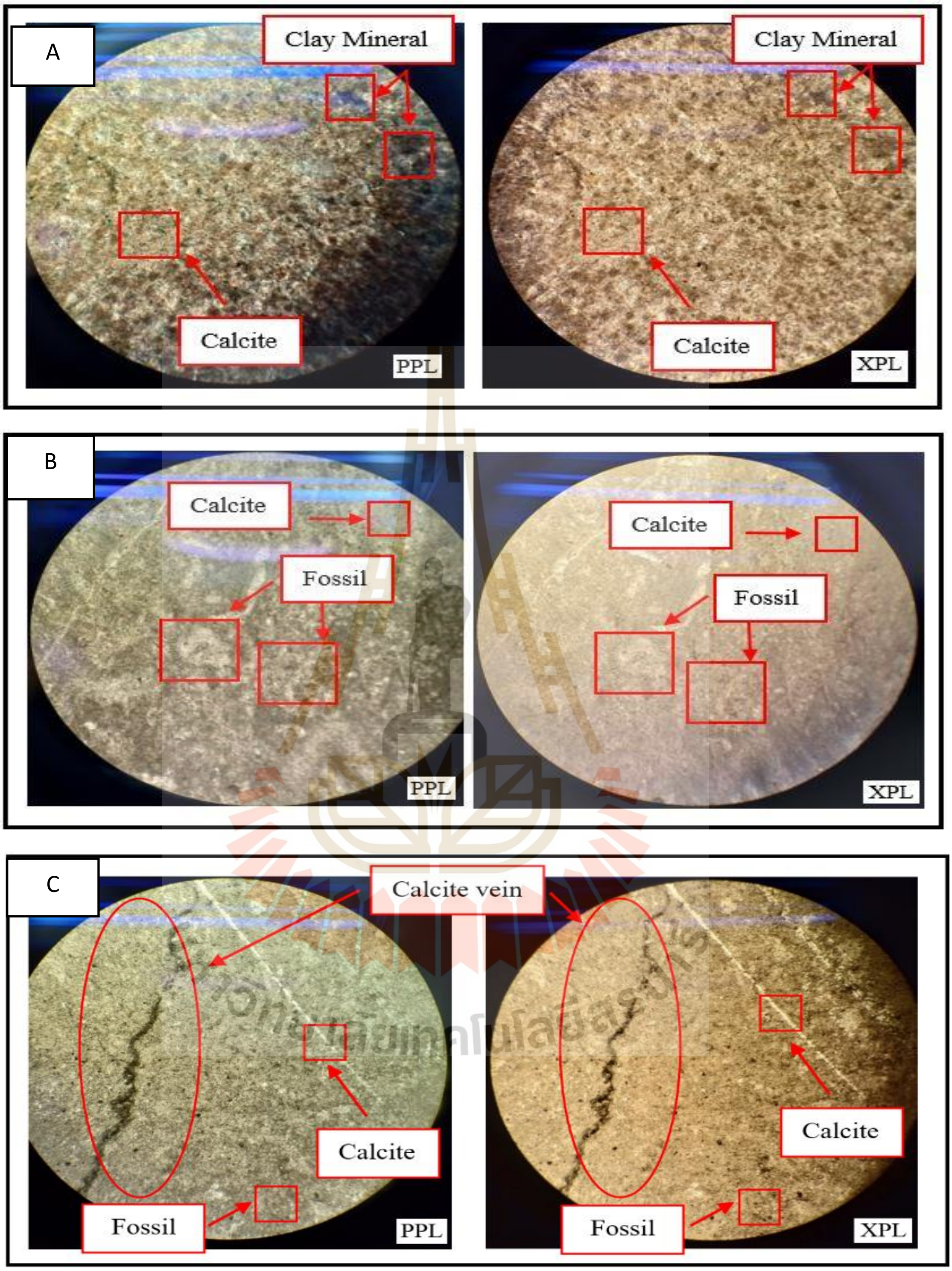
4.3.1 Physical properties before soaking with hydrochloric acid

Determination of the physical properties of Permian limestone in the northeastern region of Thailand before acid soaking was done by making a thin section. Determination porosity by Porosimeter and finding micro-structure pore by scanning electron microscope (SEM).

4.3.1.1 Petrography of thin section.

Three formations of Permian limestone petrography mainly showed the calcite and some clay mineral and quartz in the groundmass. The detail of each formation petrography as bellowed:

Petrography of Pha Nok Khao Formation mainly has the clay mineral dispersed with the calcite groundmass about 90% and found small cracks in the texture (Figure 4.9 A). Khao Khad Formation demonstrated the fossils dispersed in calcite-based rocks and found the clay mineral (Figure 4.9 B**).** Nam Mahoran Formation shows the calcite vein that has been cut with the calcite and found the fossil distribution (Figure 4.9 C).



Note: plane polarized light (PPL), and (B) crossed polarized light (XPL)

Figure 4.9 Petrography of thin section; (A) Pha Nok Khao, (B) Khao Khad, and (C) Nam Mahoran Formation.

4.3.1.2 Porosity determination

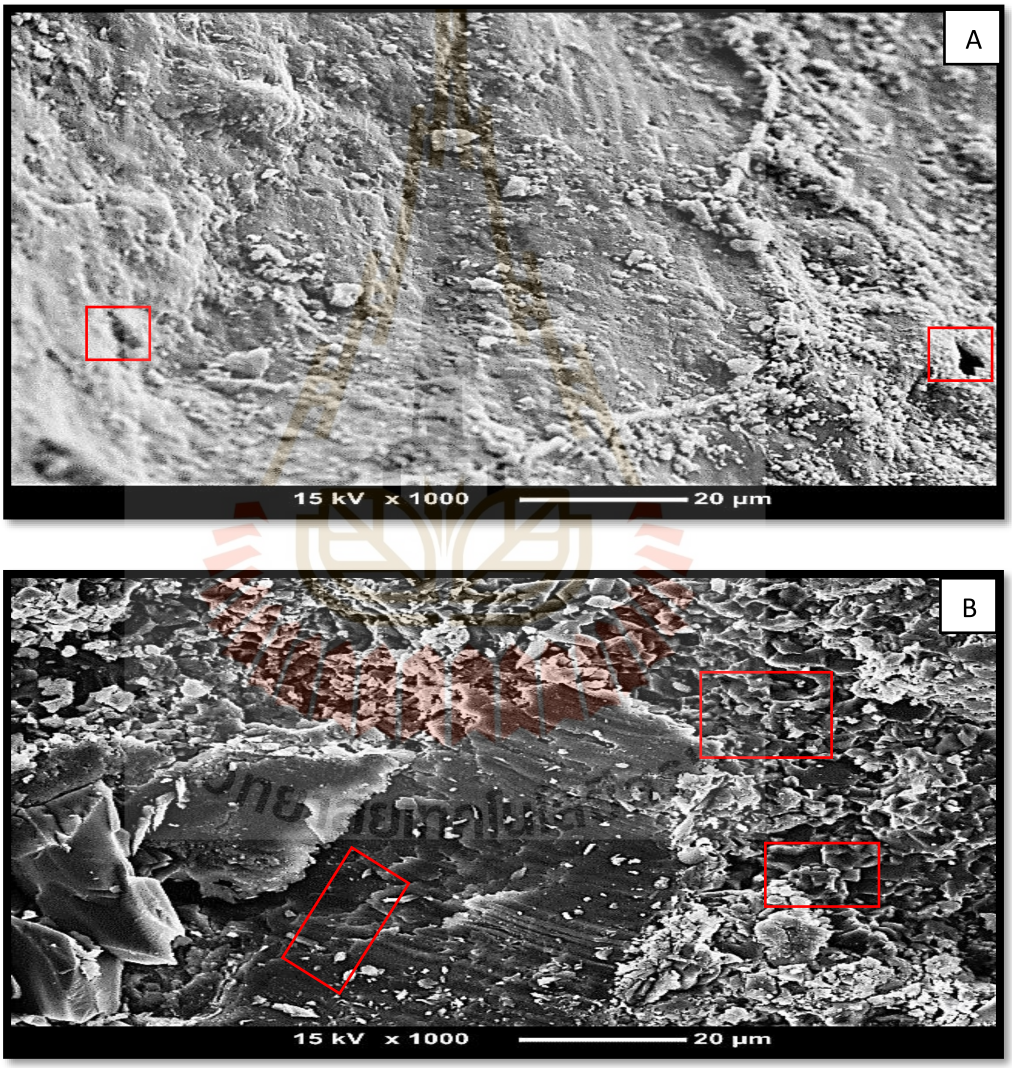
The results of the porosity values of all three Permian limestone formations before soaking with hydrochloric acid are shown in Table 4.1. Each four core samples of Pha Nok Khao, Khao Khad, and Nam Mahoran Formation from has an average porosity of 3.42%, 2.94%, and 3.47%, respectively. The porosity of Pha Nok Khao and Nam Mahoran Formation is similar value, which greater than Khao Khad Formation.

Table 4.1 Porosity result of northeastern Permian limestone formation before soaking with HCl by porosimeter.

Samples	Porosity (%)	Average Porosity (%)
Pha Nok Khao 1 (P1)	3.87	3.42
Pha Nok Khao 2 (P2)	3.60	
Pha Nok Khao 3 (P3)	2.79	
Pha Nok Khao 4 (P4)	3.41	
Pha Nok Khao 5 (P5)	3.56	
Khao Khad 1 (K1)	3.12	2.94
Khao Khad 2 (K2)	2.55	
Khao Khad 3 (K3)	2.97	
Khao Khad 4 (K4)	3.11	
Khao Khad 5 (K5)	3.04	
Nam Mahoran 1 (N1)	3.63	3.47
Nam Mahoran 2 (N2)	3.13	
Nam Mahoran 3 (N3)	3.54	
Nam Mahoran 4 (N4)	3.58	
Nam Mahoran 5 (N5)	3.47	

4.3.1.3 Scanning electron microscope (SEM)

The result of the scanning electron microscope (SEM) of Pha Nok, Khao Khao Khad, and Nam Mahoran Formation as respectively shown in Figure 4.10 (A), (B), and (C). The characteristic of the Permian limestone texture showed a few pores that represents in the red highlight, which small porosity is isolate porosity.



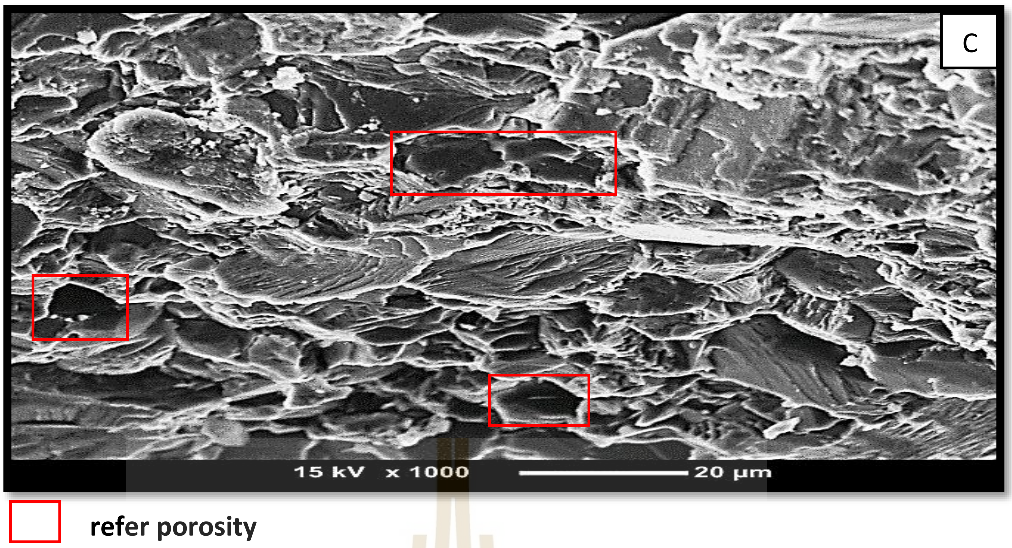


Figure 4.10 Morphology of each Permian limestone formation by SEM; (A) Pha Nok Khao, (B) Khao Khad, and (C) Nam Mahoran Formation.

4.3.2 Physical properties after soaking with hydrochloric acid

The physical properties of Permian limestone in northeastern Thailand after HCl acid soaking were tested the porosity by porosimeter and the micro-structure pore by scanning electron microscope (SEM).

4.3.2.1 Porosity determination

The results of the porosity values of all three Permian limestone formations after soaking with hydrochloric acid are shown in Table 4.2**,** Figure 4.11 and 4.12**.**

The Pha Nok Khao Formation has an average porosity of 3.41% of the non- HCl. The porosity increases of 6.71%, 7.5%, and 8.89% after soaked with 5%, 10%, and 15% HCl, respectively. The morphology result of Pha Nok Khao Formations represents the few and small sizes of pores in original rock (non-HCl). After dissolving with 5%, 10%, and 15% of HCl, the characteristic of pores is more increased and bigger size than non-HCl. The result of pore percentage and size as non-HCl < 5%HCl < 10%HCl < 15%HCl.

The Khao Khad Formation has an average porosity of 2.93% of the non-HCl. The porosity increases to 6.35%, 7.61%, and 8.72% after soaked with 5 %, 10%, and 15% HCl, respectively. The morphology result of Khao Khad Formations represents the few and small sizes of pores in original rock (non-HCl). After dissolving with 5%, 10%, and 15% of HCl, the characteristic of pores is more increased and bigger size than non-HCl. The result of pore percentage and size as non-HCl < 5%HCl < 10%HCl < 15%HCl.

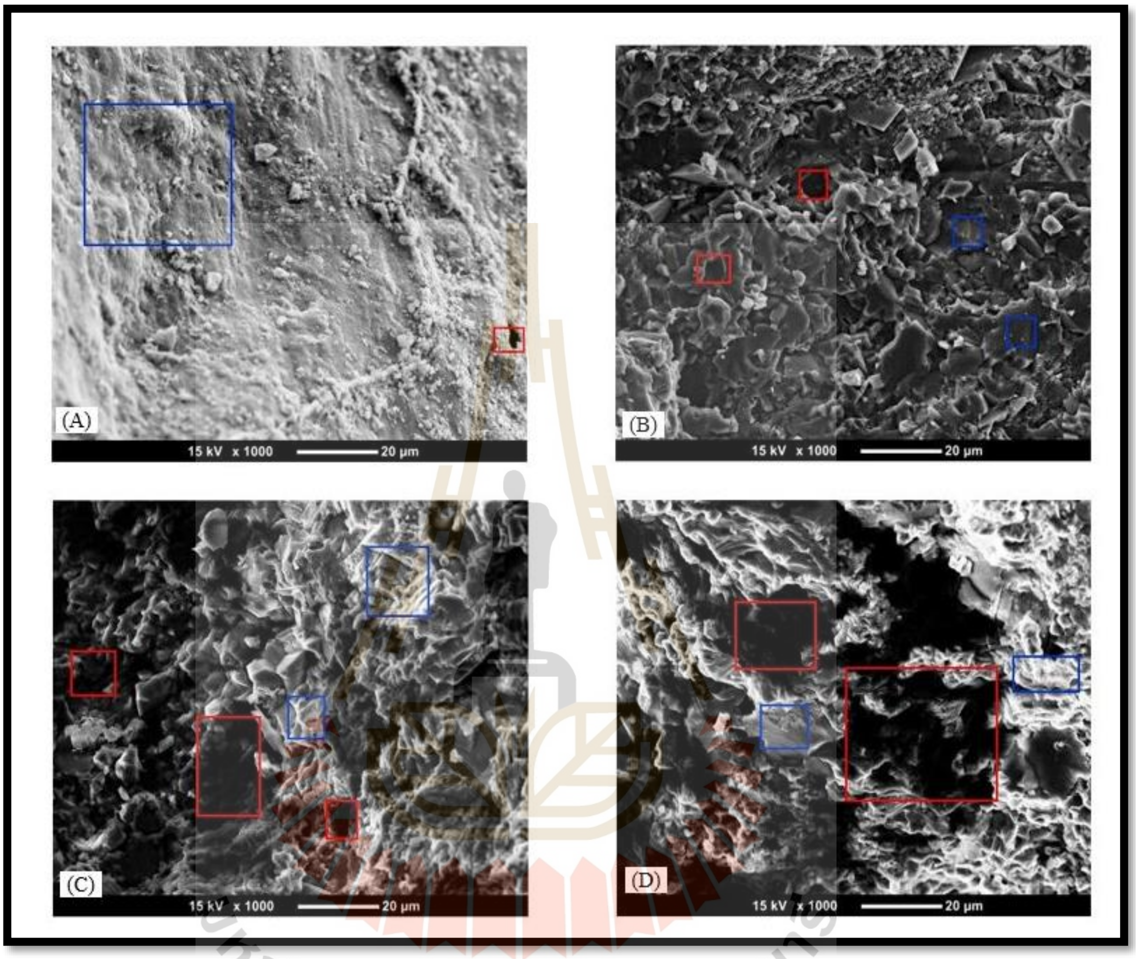
The Nam Mahoran Formation has an average porosity of 3.47% of the non-HCl acid. The porosity increases by 6.44%, 7.25%, and 7.68% after soaked with 5 %, 10%, and 15% of HCl, respectively. The morphology result of Nam Mahoran Formation represents the few and small sizes of pores in original rock (non-HCl). After dissolving with 5%, 10%, and 15% of HCl, the characteristic of pores is more increased and bigger size than non-HCl. The result of pore percentage and size as non-HCl < 5%HCl < 10%HCl < 15%HCl.

Table 4.2 Porosity result of Permian limestone and the rate of increase by using porosimeter.

Sample	Porosity n (%)					Rate of increase (%)
	Non-HCl	HCl 5%	HCl 10%	HCl 15%	HCl 20%	
Pha Nok Khao 1 (P1)	3.87	-	-	-	-	-
Pha Nok Khao 2 (P2)	3.60	6.71	-	-	-	46.34
Pha Nok Khao 3 (P3)	2.79	-	7.51	-	-	62.86
Pha Nok Khao 4 (P4)	3.41	-	-	8.899	-	61.68
Pha Nok Khao 5 (P5)	3.56	-	-	-	7.72	53.88
Khao Khad 1 (K1)	3.12	-	-	-	-	-
Khao Khad 2 (K2)	2.55	6.36	-	-	-	59.86
Khao Khad 3 (K3)	2.97	-	7.62	-	-	61.05
Khao Khad 4 (K4)	3.11	-	-	8.73	-	64.37
Khao Khad 5 (K5)	3.04	-	-	-	7.94	61.71
Nam Mahoran 1 (N1)	3.63	-	-	-	-	-
Nam Mahoran 2 (N2)	3.13	6.44	-	-	-	51.37
Nam Mahoran 3 (N3)	3.54	-	7.25	-	-	51.22
Nam Mahoran 4 (N4)	3.58	-	-	7.69	-	53.44
Nam Mahoran 5 (N5)	3.47	-	-	-	7.30	52.46

4.3.2.2 Scanning electron microscope (SEM)

The result of the scanning electron microscope (SEM) of Pha Nok Khao Formation after soaked with 5 %, 10%, and 15% of HCl comparison with non- HCl, respectively as shown in Figure 4.11 where the blue highlight area is the matrix and the area of the red highlight is the pore inside the texture.



refer porosity refer matrix

Figure 4.11 The scanning electron microscope (SEM) of Pha Nok Khao Formation after soaked with 5 %, 10%, and 15% of HCl comparison with non- HCl.

The result of the scanning electron microscope (SEM) of Nam Mahoran Formation after soaked with 5 %, 10%, and 15% of HCl, respectively as shown in

Figure 4.12. The size of the pore increases as the concentration of hydrochloric acid increases when compared to not soaking acid.

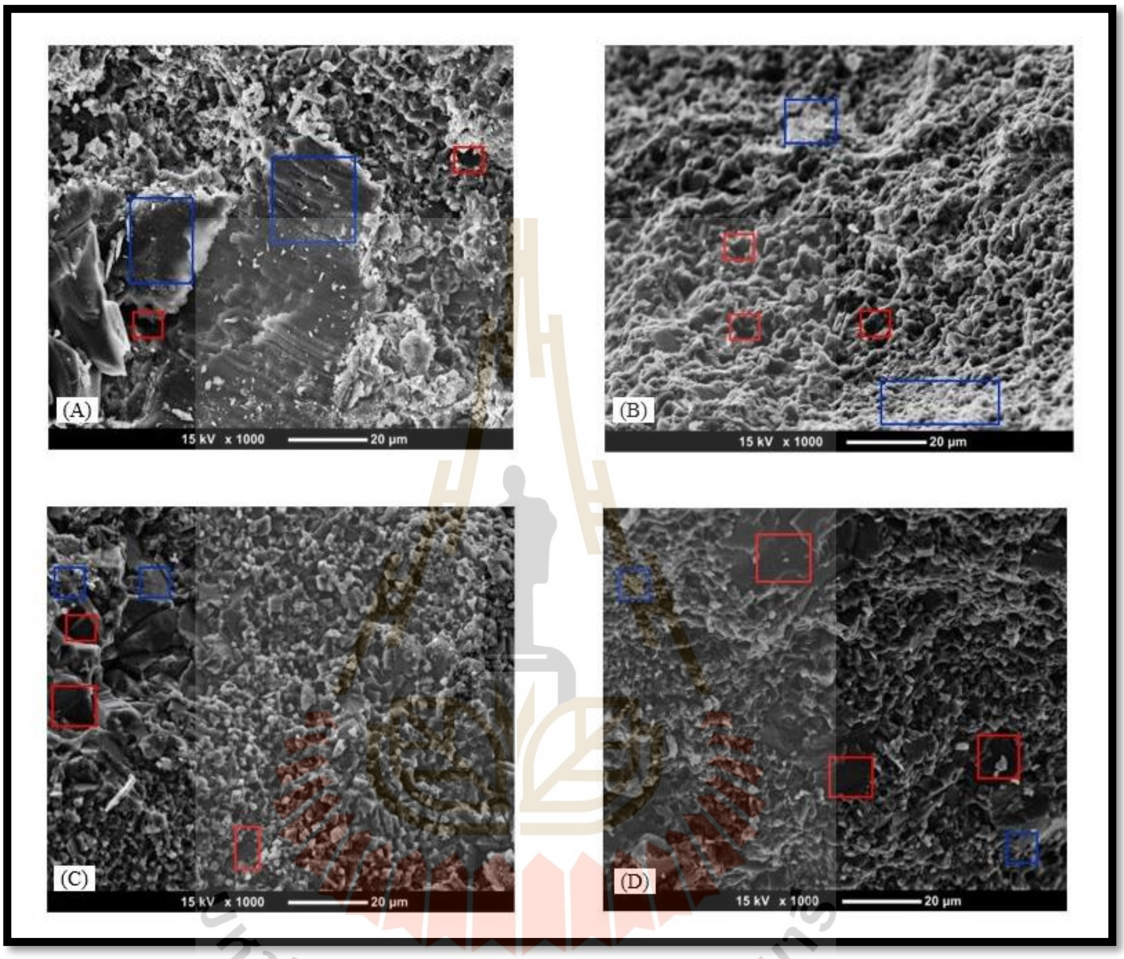


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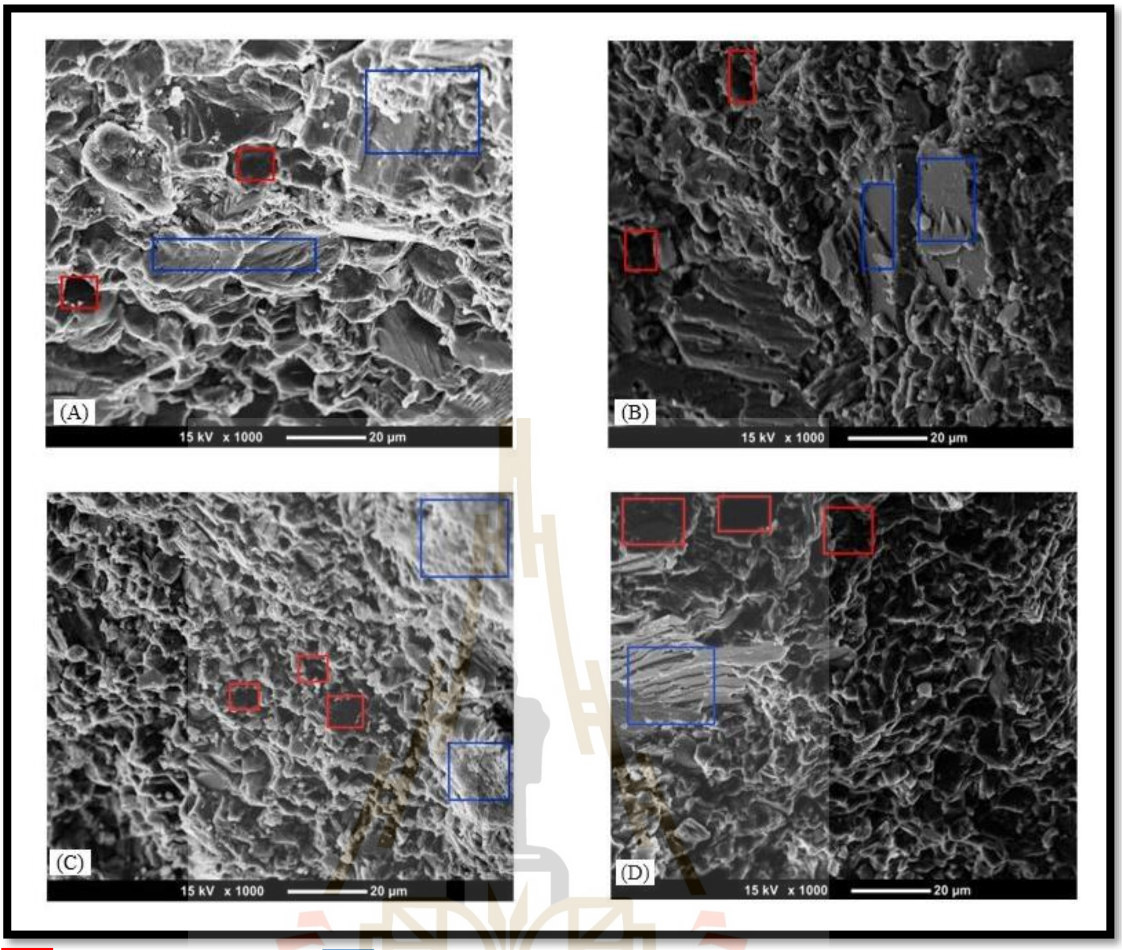
Figure 4.12 The scanning electron microscope (SEM) of Nam Mahoran Formation after soaked with 5 %, 10%, and 15% of HCl comparison with non- HCl.

The result of the scanning electron microscope (SEM) of Khao Khad Formation after soaked with 5 %, 10%, and 15% of HCl, respectively as shown in Figure 4.13. The characteristics of the limestone have an expanded pore, which varies with the increasing concentration of hydrochloric acid represents in the red highlight.



refer porosity   refer matrix

Figure 4.13 The scanning electron microscope (SEM) of Khao Khad Formation after soaked with 5 %, 10%, and 15% of HCl.

4.4 Summary of chemical and physical properties of Permian limestone both before and after soaking HCl acid

The physical and chemical properties result of Permian limestone of Pha Nok Khao, Nam Mahoran, Khao Khad Formation in northeastern Thailand dissolution with HCl acid can be summarized as Table 4.3, 4.4, and 4.5, respective.

The porosity result of all three formations found that the increasing porosity according to the acid concentration. After dissolving with 5%, 10%, 15% and 20% of HCl, the characteristic of pores is more increased and bigger size than non-HCl. The result of pore percentage and size as non-HCl < 5%HCl < 10%HCl < 20%HCl < 15%HCl (Figure 4.14).

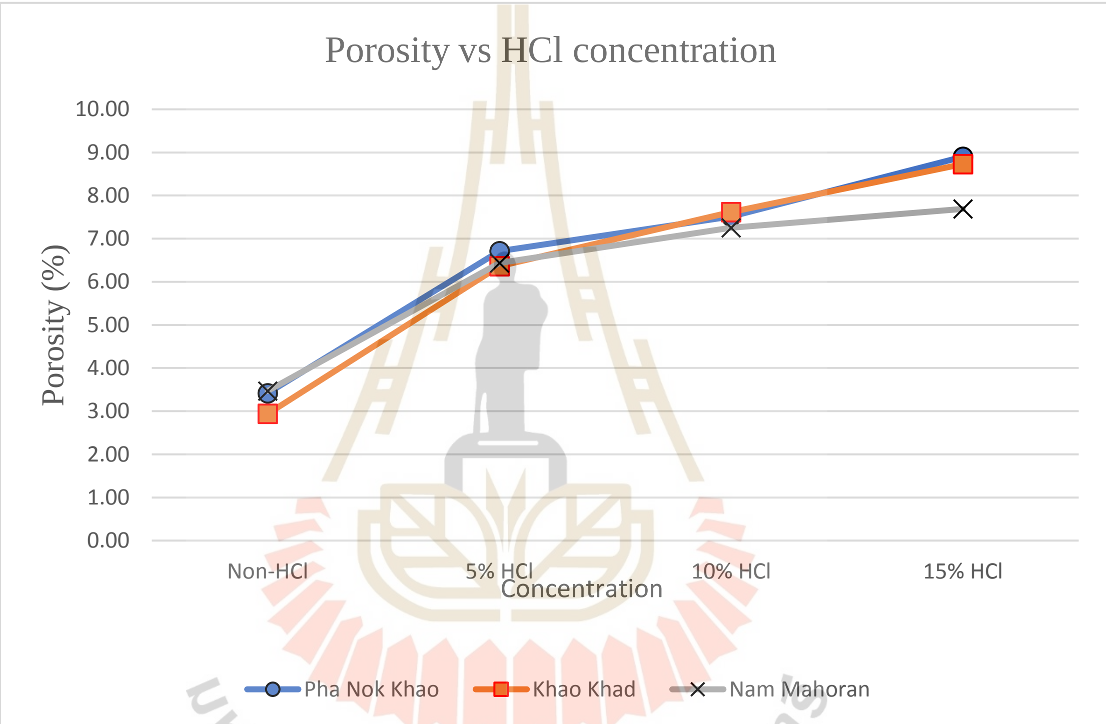


Figure 4.14 Relationship graph between porosity with HCl concentration.

Moreover, the rate of matrix dissolution depends on calcium (Ca) contents (Figure 4.15). According to Equation 2.3, the dissolution of limestone with hydrochloric acid, the main product obtained is calcium. The rate of increase in calcium intake was highest in Pha Nok Khao Formation, followed by Khao Khad Formation and Nam Mahoran Formation, respectively. Corresponding to the effect of the porosity at

Pha Nok Khao Formation have the porosity increased the highest, followed by Khao Khad Formation and Nam Mahoran Formation, respectively.

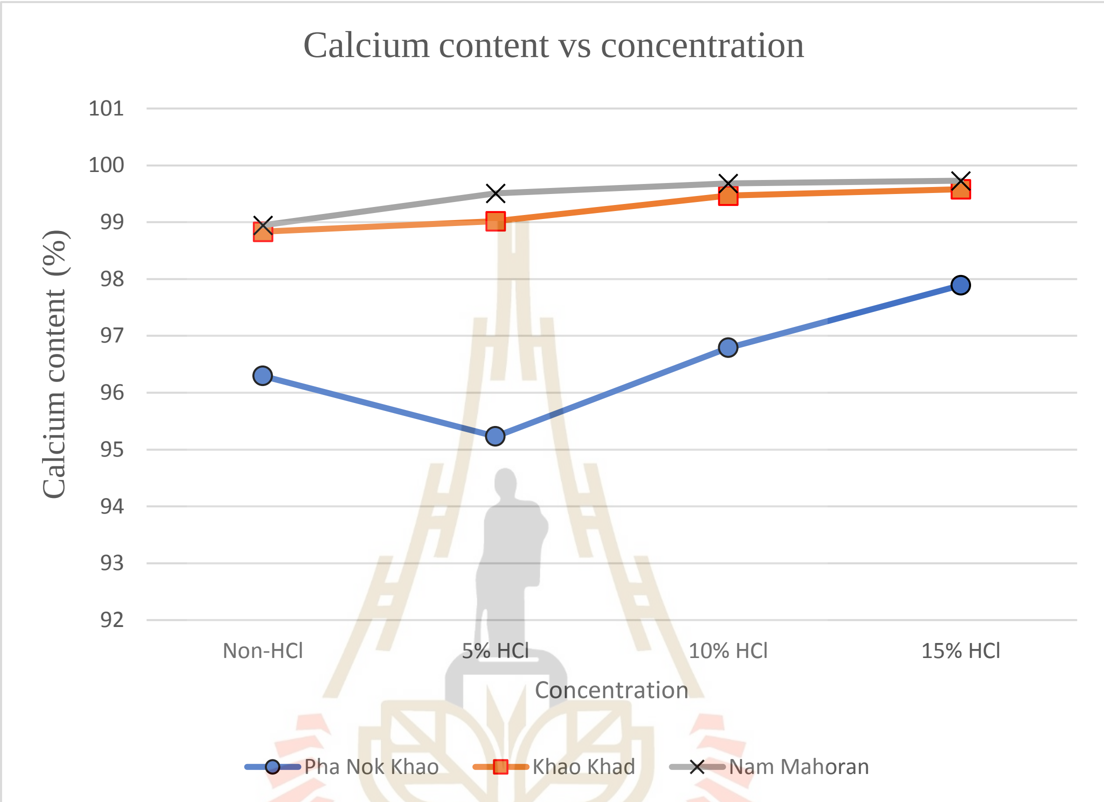


Figure 4.15 Relationship graph between calcium content with HCl concentration.

Table 4.3 Summary of the chemical and phyical properties of Pha Nok Khao Formation in northeastern Thailand (Continued)

Sample	Sample No.	Concentrations	Physical property				Chemical property	
			Ø Before (%)	Ø After (%)	Rate of increase (%)	SEM	XRD	XRF
Pha Nok Khao Formation	P1	Non-HCl	3.87	3.87	-	The morphology result of Pha Nok Khao Formations represents the few and small sizes of pores in original rock (non-HCl). After dissolving with 5%, 10%, and 15% of HCl, the characteristic of pores is more increased and bigger size than non-HCl. The result of pore percentage	Calcite Quartz	Al_2O_3 = 0.63% SiO_2 = 1.51% K_2O = 0.07% CaO = 96.29% TiO_2 = 0.07% Fe_2O_3 = 0.99% SrO = 0.43%
	P2	5% HCl	3.60	6.71	46.33		Calcite Quartz	K_2O = 0.05% CaO = 95.23% MnO_2 = 0.46% SiO_2 = 1.31% Fe_2O_3 = 2.23% SrO = 0.73%

Table 4.3 Summary of the chemical and phyical properties of Pha Nok Khao Formation in northeastern Thailand (Continued)

Sample	Sample No.	Concentrations	Physical property				Chemical property	
			Ø Before (%)	Ø After (%)	Rate of increase (%)	SEM	XRD	XRF
	P3	10% HCl	2.79	7.50	62.86	and size as non-HCl < 5%HCl < 10%HCl < 15%HCl.	Calcite Dolomite	K2O = 0.05% CaO = 96.79% MnO2 = 0.16% Fe2O3 = 2.23% SrO = 0.77%
	P4	15% HCl	3.41	8.89	61.67		Calcite Dolomite	K2O = 0.05% CaO = 97.89% MnO2 = 1.45% Fe2O3 = 1.45 % SrO = 0.50%
	P5	20% HCl	3.56	7.72	53.88	-	-	-

Table 4.4 Summary of the chemical and physical properties of Khao Khad Formation in northeastern Thailand.

Sample	Sample No.	Concentrations	Physical property				Chemical property	
			Ø Before (%)	Ø After (%)	Rate of increase (%)	SEM	XRD	XRF
Khao Khad Formation	K1	Non-HCl	3.12	3.12	-	The morphology result of Khao Khad Formations represents the few and small sizes of pores in original rock (non-HCl). After dissolving with 5%, 10%, and 15% of HCl, the characteristic of pores is more increased and bigger size than non-HCl. The result of pore percentage and size as non-HCl < 5%HCl < 10%HCl < 15%HCl.	Calcite Quartz	Al_2O_3 = 0.59% K_2O = 0.06% CaO = 98.83% TiO_2 = 0.06% Fe_2O_3 = 0.35% SrO = 0.11%
	K2	5% HCl	2.55	6.36	59.86		Calcite Quartz	Al_2O_3 = 0.58% CaO = 99.02% Fe_2O_3 = 0.29% SrO = 0.10%

Table 4.4 Summary of the chemical and physical properties of Khao Khad Formation in northeastern Thailand. (Continued)

Formation	Sample No.	Concentrations	Physical property				Chemical property	
			Ø Before (%)	Ø After (%)	Rate of increase (%)	SEM	XRD	XRF
Khao Khad Formation	K3	10% HCl	2.97	7.61	61.05		Calcite	K_2O = 0.07% CaO = 99.47% Fe_2O_3 = 0.35% SrO = 0.12%
	K4	15% HCl	3.11	8.72	64.37		Calcite	SO_3 = 0.05% CaO = 99.58% Fe_2O_3 = 0.27% SrO = 0.11%
	K5	20% HCl	3.04	7.94	61.71	-	-	-

Table 4.5 Summary of the chemical and physical properties of Nam Mahoran Formation in northeastern Thailand.

Sample	Sample No.	Concentrations	Physical property				Chemical property	
			Ø Before (%)	Ø After (%)	Rate of increase (%)	SEM	XRD	XRF
Nam Mahoran Formation	N1	Non-HCl	3.63	3.63	-	The morphology result of Nam Mahoran Formations represents the few and small sizes of pores in original rock (non-HCl). After dissolving with 5%, 10%, and 15% of HCl, the characteristic of pores is more increased and bigger size than non-HCl. The result of pore percentage and size as non-HCl < 5%HCl < 10%HCl < 15%HCl.	Calcite	CaO = 98.95% Fe_2O_3 = 0.92% SrO = 0.13%
	N2	5% HCl	3.13	6.44	51.36		Calcite	CaO = 99.51% Fe_2O_3 = 0.34% SrO = 0.16%
	N3	10% HCl	3.54	7.25	51.21		Calcite	CaO = 99.68% Fe_2O_3 = 0.16% SrO = 0.16%
	N4	15% HCl	3.58	7.68	53.43		Calcite	CaO = 99.73% Fe_2O_3 = 0.10% SrO = 0.17%
	N5	20% HCl	3.47	7.3	52.46		-	-

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Introduction

This chapter is divided into the main two parts consisting of conclusions and recommendations. In the conclusion part, it presents the conclusion from two main sections (I) chemical and physical property of the Permian limestone in northeastern Thailand, and (II) the efficiency of hydrochloric (HCl) acid concentration on the dissolution of limestone, respectively. In the recommendation part, it consists of some recommendations for future study.

5.2 Conclusion

Results of the physical and chemical properties and dissolution of Permian limestones such as Pha Nok Khao, Khao Khad, and Num Mahoran Formation Permian limestone formation in northeastern Thailand has been shown in Table 4.3, 4.4, and 4.5, respectively. The conclusion of this study was reached below.

5.2.1 Chemical and physical properties before dissolution with hydrochloric acid

1) Elemental and mineral compositions

The chemical properties of Permian limestone in northeastern Thailand both before and after dissolution with hydrochloric acid can be concluded the result as follows:

The calcite is mainly found in all three formations. The Nam Mahoran Formation is highly calcite with the main consist of CaO and respectively minor of SrO and Fe_2O_3. Also, the calcite is mainly found in Khao Khad and Pha Nok Khao Formation with minor quartz content. The Khao Khad Formation highly consists of CaO with respectively minor of Al_2O_3, Fe_2O_3, SrO, K_2O, and TiO_2. The Pha Nok Khao Formation mainly consists of CaO with respectively minor of SiO_2, Fe_2O_3, Al_2O_3, SrO, K_2O, and TiO_2.

2) Petrography and porosity properties

Petrography of three formations before dissolving with HCl. The Pha Nok Khao Formation mainly has the clay minerals dispersed with the calcite groundmass about 90% and found small cracks in the texture. The Khao Khad Formation demonstrated the fossils dispersed in calcite-based rocks and found the clay minerals. The Nam Mahoran Formation shows the calcite vein that has been cut with the calcite and found the fossil distribution.

Results of the porosity values before dissolving with HCl of Pha Nok Khao, Khao Khad, and Nam Mahoran Formation from has an average porosity of 3.42%, 2.94%, and 3.47%, respectively. The porosity of Pha Nok Khao and Nam Mahoran Formation is similar value, which greater than Khao Khad Formation.

5.2.2 Chemical and physical properties after dissolution with hydrochloric acid

1) Elemental and mineral compositions

Nam Mahoran Formation has been detected only calcite minerals, in which the content of calcite and CaO increases more than the original formation causing the matrix dissolution. The Khao Khad Formation after dissolved with 5% HCl detected content of quartz and calcite, while the calcite content was detected at a concentration of 10% HCl and 15% HCl. The Pha Nok Khao Formation after dissolved with 5% HCl detected content of quartz and calcite, which similar to the original sample. Meanwhile, the content of dolomite and calcite were found at a concentration of 10% HCl and 15% HCl.

The calcite and CaO contents in the Nam Mahoran Formation is greater than Khao Khad and Pha Nok Khao Formation, respectively. These content of calcite and CaO relate to the porosity and rate of matrix dissolution. The Pha Nok Khao Formation consists of the quartz and SiO_2 content resulting in the reduction of matrix dissolution.

2) Physical property

The physical properties of Permian limestone in northeastern Thailand both before and after dissolution with HCl acid were tested the porosity by porosimeter and the micro-structure pore by scanning electron microscope (SEM).

The Pha Nok Khao Formation has an average porosity of 3.41% of the non- HCl, and the morphology represents the few and small sizes of pores in the original rock. After dissolution with 5%, 10%, and 15% HCl, the increasing rate of porosity is 46.3%, 62.9%, and 61.7%, respectively. Moreover, the characteristic of pores is more increased and bigger size than non-HCl.

The Khao Khad Formation has an average porosity of 2.93% of the non-HCl, and the morphology represents the few and small sizes of pores in the original rock. After dissolution with 5%, 10%, and 15% HCl, the increasing rate of porosity is 64.4%, 59.9%, and 61.1%, respectively. The characteristic of pores is more increased and bigger size than non-HCl.

The Nam Mahoran Formation has an average porosity of 3.47% of the non-HCl, and the morphology represents the few and small sizes of pores in the original rock. After dissolution with 5%, 10%, and 15% HCl, the increasing rate of porosity is 51.4%, 52.2%, and 53.4%, respectively. After dissolving with 5%, 10%, and 15% HCl. The characteristic of pores is more increased and bigger size than non-HCl.

The result of the matrix dissolution rate depends on CaO and calcite contents. The CaO and calcite contents in Nam Mahoran Formation greater than Khao Khad and Pha Nok Khao Formation, respectively. At the 5%HCl, the rate of matrix dissolution of Khao Khad Formation is higher than Nam Mahoran and Pha Nok Khao Formation, meanwhile, the 10% and 15% HCl represented Pha Nok Khao is higher than Khao Khad and Nam Mahoran Formations.

Morphology results of Pha Nok Khao, Khao Khad, and Nam Mahoran Formations represent the few and small sizes of pores in original rock (non-HCl). After dissolving with 5%, 10%, and 15% of HCl, the characteristic of pores is more increased and bigger size than non-HCl. The result of pore percentage and size as non-HCl < 5%HCl < 10%HCl < 15%HCl. This porosity increased after HCl dissolving with the greatest increase at 15% acid concentration and the Permian limestone in northeastern Thailand with the highest increase in porosity were those of Pha Nok Khao Formation, followed by Khao Khad and Nam Mahoran Formation, respectively. Therefore, the 15% HCl concentration is the best dissolution efficiency of all three Permian formations in northeastern Thailand, followed by 10% concentration and 5% concentration, respectively.

5.3 Recommendations

The research, experimental and results lead to recommendation area for further studies including

- It should be tested all of the samples with another method such as permeability, detailed fossil analysis, etc.
- It should be more expand the scope of sample collection for testing
- It should be tested all of the samples in real conditions under the factors of temperature and pressure.
- It should be studied under other conditions and factors such as time of dissolution with HCl, temperature and pressure test, rate of dissolution, etc.
- It should be analyzed the solution after sample dissolution to evaluate the impact of the solution on the environment.
- Test the amount of acid to be used, compare it with the price, and see the economic suitability and the effect of corrosion problems.

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APPENDIX A

EXPERIMENTAL DATA

Elemental composition

Table A1 Result of Pha Nok Khao Formation from X-ray Fluorescence method.

Pha Nok Khao Formation					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
Al	0.336	0.347	Al_2O_3	0.634	0.353
Si	0.704	0.699	SiO_2	1.505	1.423
K	0.062	0.044	K_2O	0.074	0.045
Ca	68.821	47.899	CaO	96.294	97.54
Ti	0.043	0.025	TiO_2	0.072	0.051
Fe	0.693	0.346	Fe_2O_3	0.991	0.353
Sr	0.363	0.115	SrO	0.429	0.235
O	28.979	50.524			

Table A2 Result of Nam Mahoran Formation from X-ray Fluorescence method.

Nam Mahoran Formation					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
Ca	70.716	49.559	CaO	98.946	99.602
Fe	0.643	0.323	Fe_2O_3	0.92	0.325
Sr	0.114	0.036	SrO	0.134	0.073
O	28.527	50.081			

Table A3 Result of Khao Khad Formation from X-ray Fluorescence method.

Khao Khad Formation					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
Al	0.312	0.324	Al_2O_3	0.59	0.327
K	0.052	0.038	K_2O	0.063	0.038
Ca	70.636	49.355	CaO	98.834	99.413
Ti	0.035	0.021	TiO_2	0.059	0.041
Fe	0.243	0.122	Fe_2O_3	0.347	0.123
Sr	0.091	0.029	SrO	0.107	0.058
O	28.631	50.112			

Table A4 Result of Khao Khad Formation from X-ray Fluorescence method after soaking with 5% HCl.

Khao Khad Formation with 5% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
Al	0.307	0.319	Al_2O_3	0.581	0.321
Ca	70.771	49.445	CaO	99.023	99.519
Fe	0.204	0.102	Fe_2O_3	0.292	0.103
Sr	0.088	0.028	SrO	0.104	0.057
O	28.629	50.105			

Table A5 Result of Khao Khad Formation from X-ray Fluorescence method after soaking with 10% HCl.

Khao Khad Formation with 10% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
K	0.028	0.025	K_2O	0.07	0.049
Ca	71.092	49.768	CaO	99.472	99.769
Fe	0.245	0.123	Fe_2O_3	0.351	0.124
Sr	0.091	0.029	SrO	0.107	0.058
O	28.544	50.055			

Table A6 Result of Khao Khad Formation from X-ray Fluorescence method after soaking with 10% HCl.

Khao Khad Formation with 15% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
S	0.019	0.017	SO_3	0.048	0.034
Ca	71.166	49.818	CaO	99.575	99.814
Fe	0.19	0.096	Fe_2O_3	0.272	0.096
Sr	0.089	0.028	SrO	0.105	0.057
O	28.536	50.041			

Table A7 Result of Pha Nok Khao Formation from X-ray Fluorescence method after soaking with 5% HCl.

Pha Nok Khao Formation with 5% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
K	0.039	0.008	K_2O	0.047	0.028
Ca	65.199	47.728	CaO	95.233	82.528
Mn	0.1	0.048	MnO_2	0.456	0.105
Si	0.704	0.699	SiO_2	1.305	1.423
Fe	1.563	0.74	Fe_2O_3	2.234	0.809
Sr	0.643	0.195	SrO	0.725	0.427
O	31.752	50.582			

Table A8 Result of Pha Nok Khao Formation from X-ray Fluorescence method after soaking with 10% HCl.

Pha Nok Khao Formation with 10% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
K	0.039	0.008	K_2O	0.047	0.028
Ca	66.02	45.094	CaO	96.796	98.631
Mn	0.1	0.048	MnO_2	0.158	0.105
Fe	0.563	0.74	Fe_2O_3	2.234	0.809
Sr	0.647	0.195	SrO	0.765	0.427
O	32.631	53.915			

Table A9 Result of Pha Nok Khao Formation from X-ray Fluorescence method after soaking with 15% HCl.

Pha Nok Khao Formation with 15% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
K	0.039	0.008	K_2O	0.047	0.028
Ca	69.96	0.015	CaO	97.888	99.107
Mn	0.073	0.007	MnO_2	0.116	0.076
Fe	1.016	0.01	Fe_2O_3	1.453	0.516
Sr	0.42	0.004	SrO	0.497	0.272
O	28.492	0.009			

Table A10 Result of Nam Mahoran Formation from X-ray Fluorescence method after soaking with 5% HCl.

Nam Mahoran Formation with 5% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
Ca	71.115	49.809	CaO	99.505	99.796
Fe	0.237	0.119	Fe_2O_3	0.338	0.119
Sr	0.133	0.043	SrO	0.157	0.085
O	28.515	50.03			

Table A11 Result of Nam Mahoran Formation from X-ray Fluorescence method after soaking with 10% HCl.

Nam Mahoran Formation with 10% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
Ca	71.241	49.887	CaO	99.68	99.857
Fe	0.111	0.056	Fe_2O_3	0.159	0.056
Sr	0.136	0.044	SrO	0.161	0.087
O	28.512	50.014			

Table A12 Result of Nam Mahoran Formation from X-ray Fluorescence method after soaking with 15% HCl.

Nam Mahoran Formation with 15% HCl.					
Elem.	Mass (%)	Atomic (%)	Formula	Mass (%)	Molecule (%)
Ca	71.279	49.911	CaO	99.734	99.875
Fe	0.07	0.035	Fe_2O_3	0.1	0.035
Sr	0.14	0.045	SrO	0.166	0.09
O	28.511	50.009			

Table A13 Result of Nam Mahoran Formation from X-ray Fluorescence

Samples	**Porosity (%)**	**Average Porosity (%)**
Nam Mahoran 1	3.63062	3.47055525
Nam Mahoran 2	3.132974	
Nam Mahoran 3	3.538394	
Nam Mahoran 4	3.580233	
Pha Nok Khao 1	3.870927	3.41766925
Pha Nok Khao 2	3.602728	
Pha Nok Khao 3	2.788604	
Pha Nok Khao 4	3.408418	
Khao Khad 1	3.123772	2.93812875
Khao Khad 2	3.109829	
Khao Khad 3	2.552767	
Khao Khad 4	2.966147	

Table A14 Porosity result of Permian limestone and the rate of increase by using porosimeter.

Sample	Porosity n (%)				Rate of increase (%)
	Non-HCl	HCl 5%	HCl 10%	HCl 15%	
Nam Mahoran 1	3.63062	-	-	-	-
Nam Mahoran 2	3.132974	6.442137	-	-	51.36747325
Nam Mahoran 3	3.538394	-	7.253071	-	51.21523007
Nam Mahoran 4	3.580233	-	-	7.688834	53.4359436
Pha Nok Khao 1	3.870927	-	-	-	-
Pha Nok Khao 2	3.602728	6.713473	-	-	46.33585329
Pha Nok Khao 3	2.788604	-	7.508601	-	62.8612041
Pha Nok Khao 4	3.408418	-	-	8.89393	61.67703141
Khao Khad 1	3.123772	-	-	-	-
Khao Khad 2	3.109829	-	-	8.726907	64.36504938
Khao Khad 3	2.552767	6.359537	-	-	59.85923189
Khao Khad 4	2.966147	-	7.615892	-	61.05318983

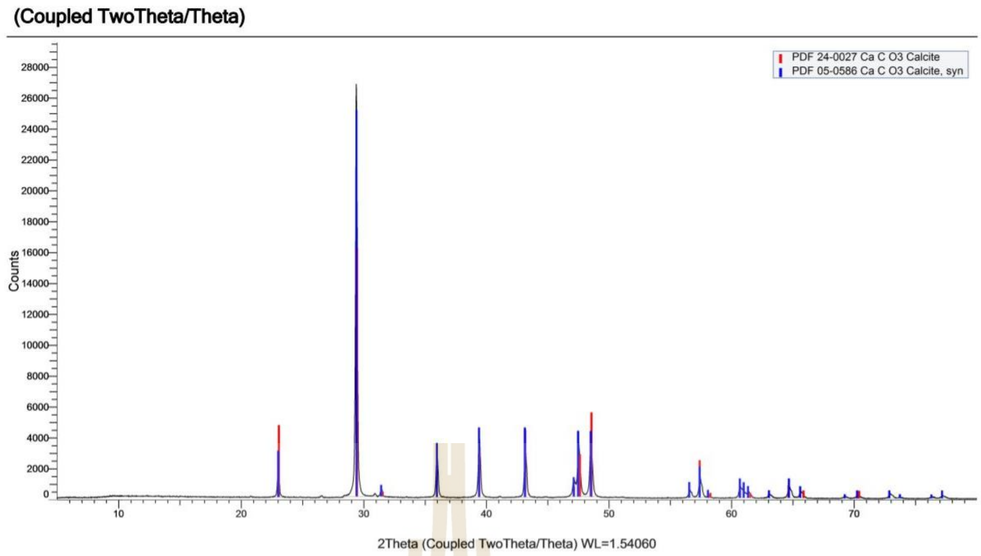

Figure A1. The graph shows the angle of theta which indicates the mineral that exists in the Khao Khad Formation.

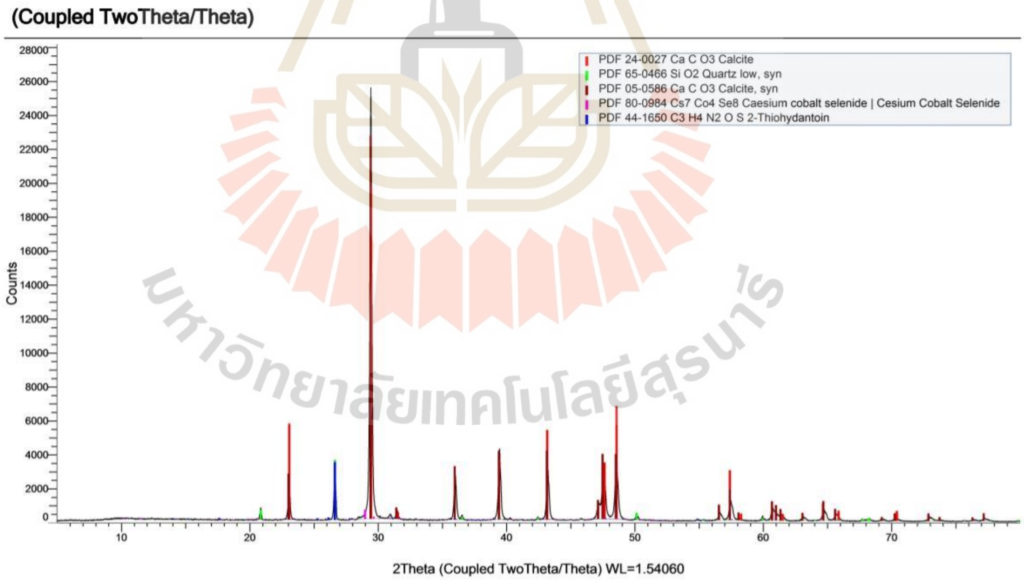

Figure A2. The graph shows the angle of theta which indicates the mineral that exists in the Nam Mahoran Formation.

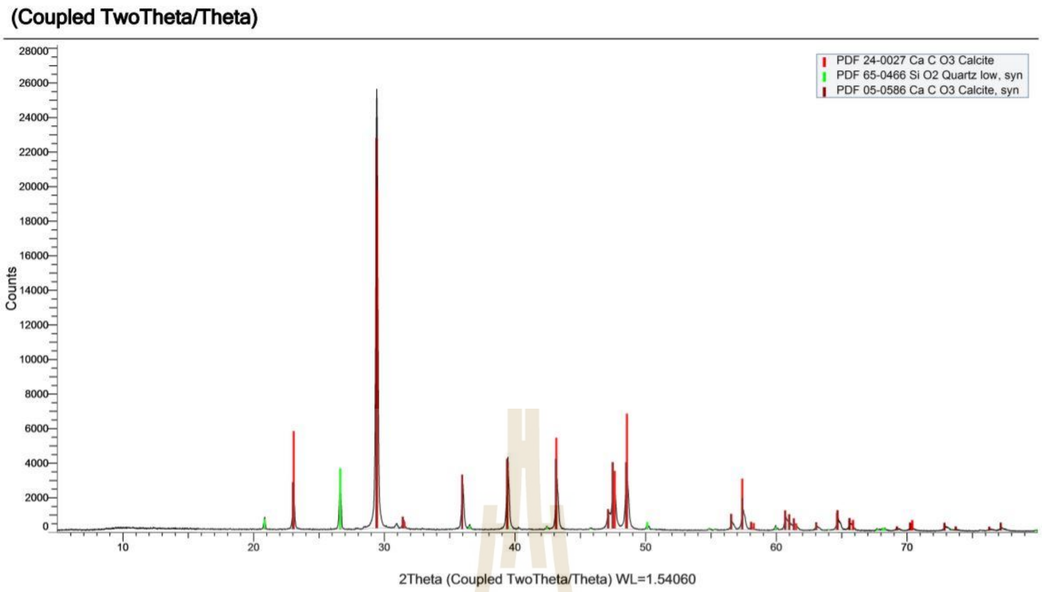

Figure A3. The graph shows the angle of theta which indicates the mineral that exists in the Pha Nok Khao Formation

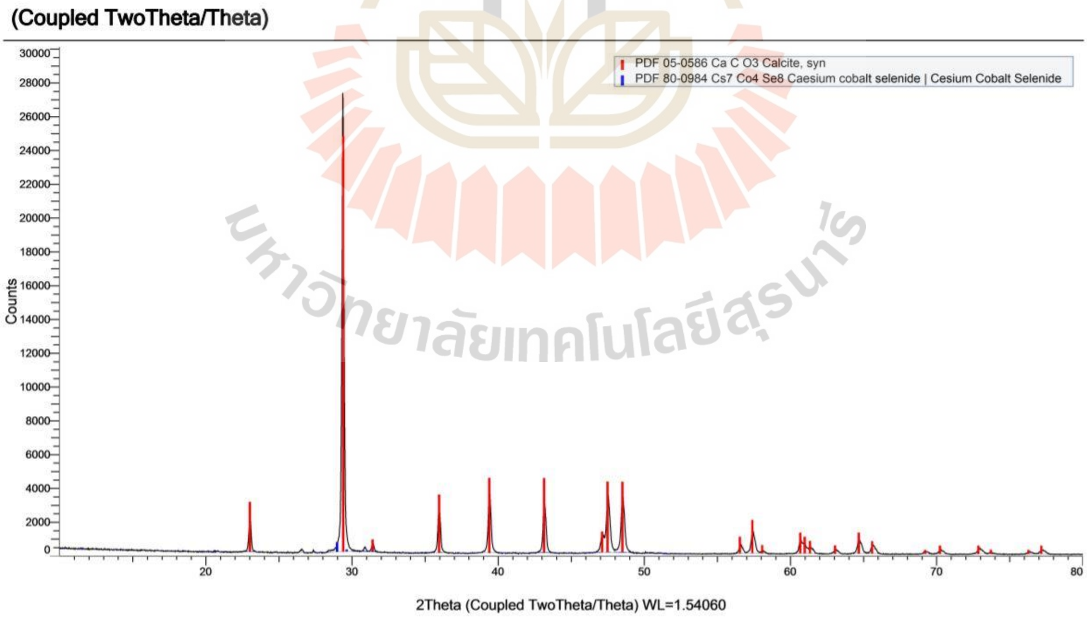

Figure A4. The graph shows the angle of theta which indicates the mineral that exists in the Khao Khad Formation after soaking with 5 % HCl.

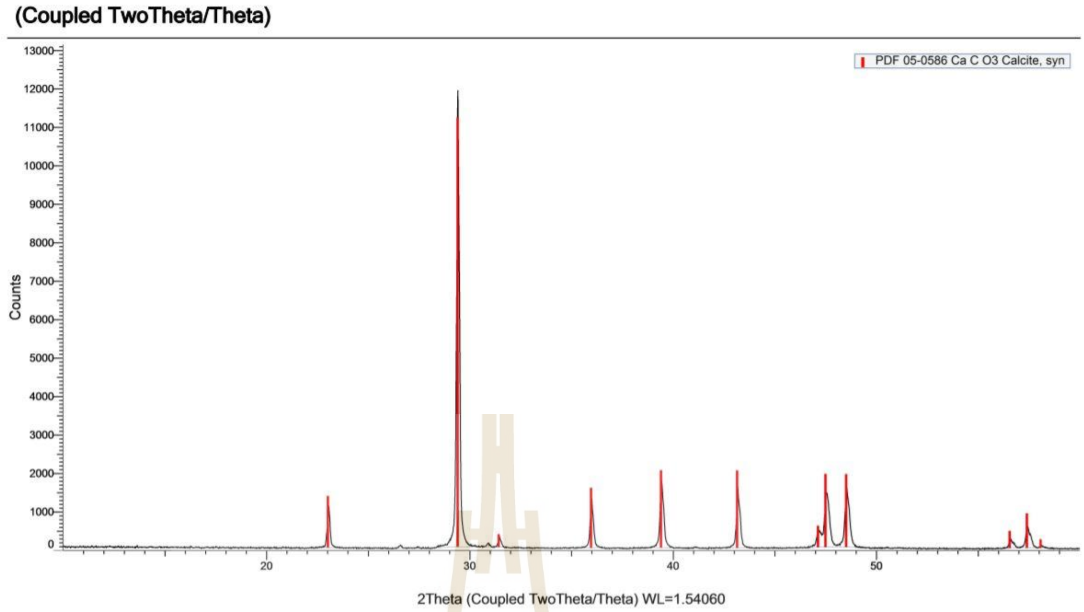

Figure A5. The graph shows the angle of theta which indicates the mineral that exists in the Khao Khad Formation after soaking with 10 % HCl.

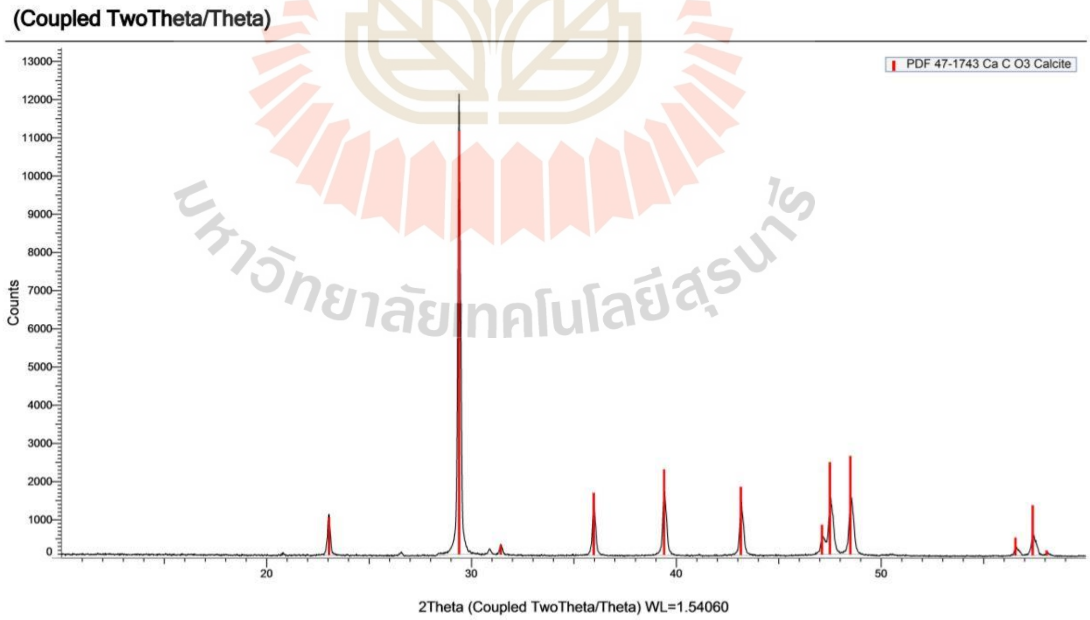

Figure A6. The graph shows the angle of theta which indicates the mineral that exists in the Khao Khad Formation after soaking with 15 % HCl.

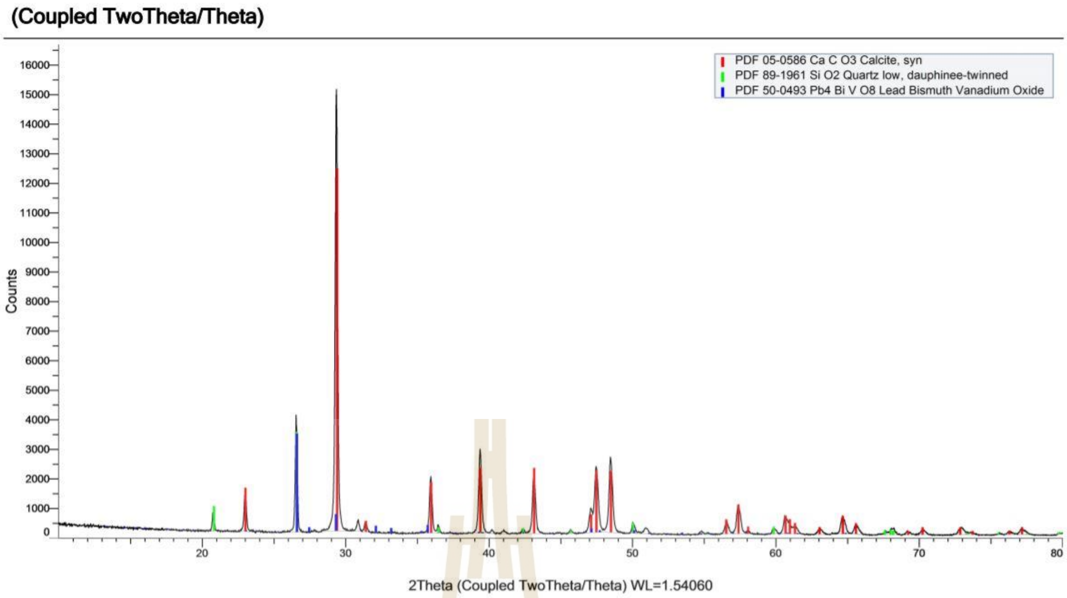

Figure A7. The graph shows the angle of theta which indicates the mineral that exists in the Pha Nok Khao Formation after soaking with 5 % HCl.

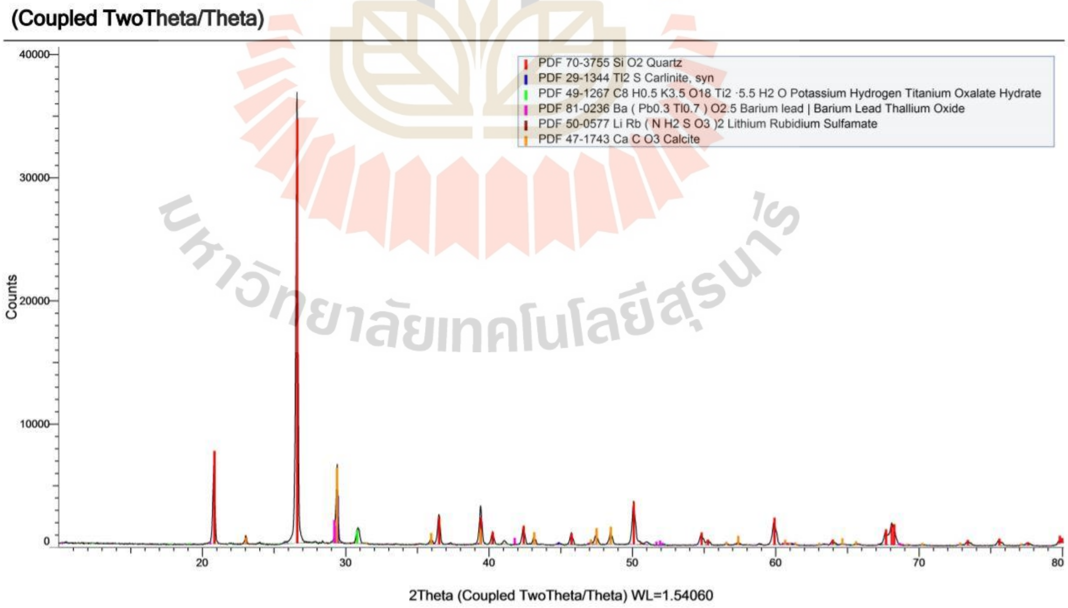

Figure A8. The graph shows the angle of theta which indicates the mineral that exists in the Pha Nok Khao Formation after soaking with 10% HCl.

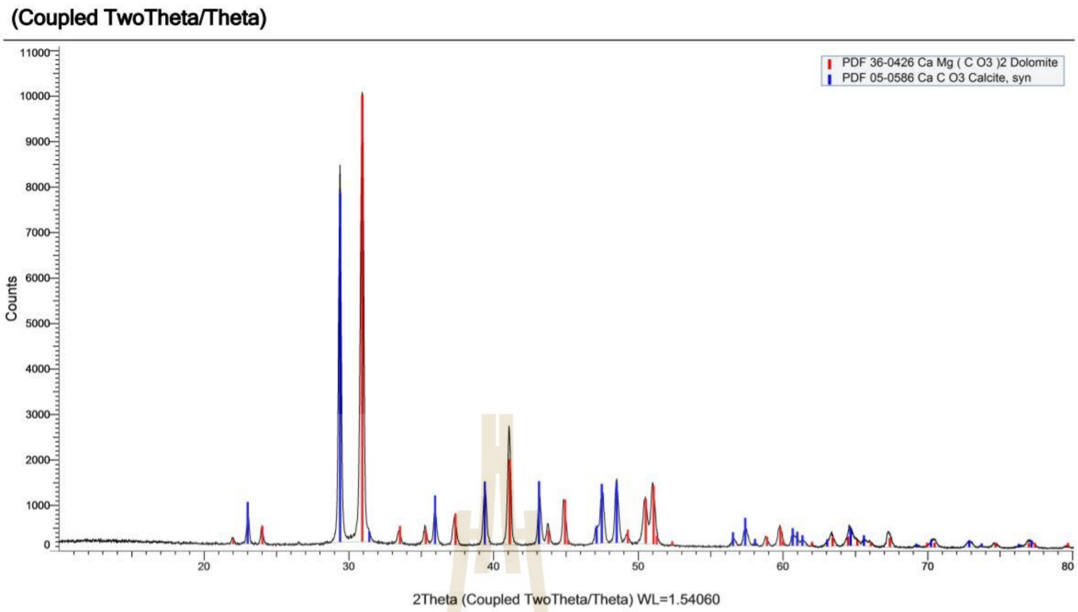

Figure A9. The graph shows the angle of theta which indicates the mineral that exists in the Pha Nok Khao Formation after soaking with 15% HCl.

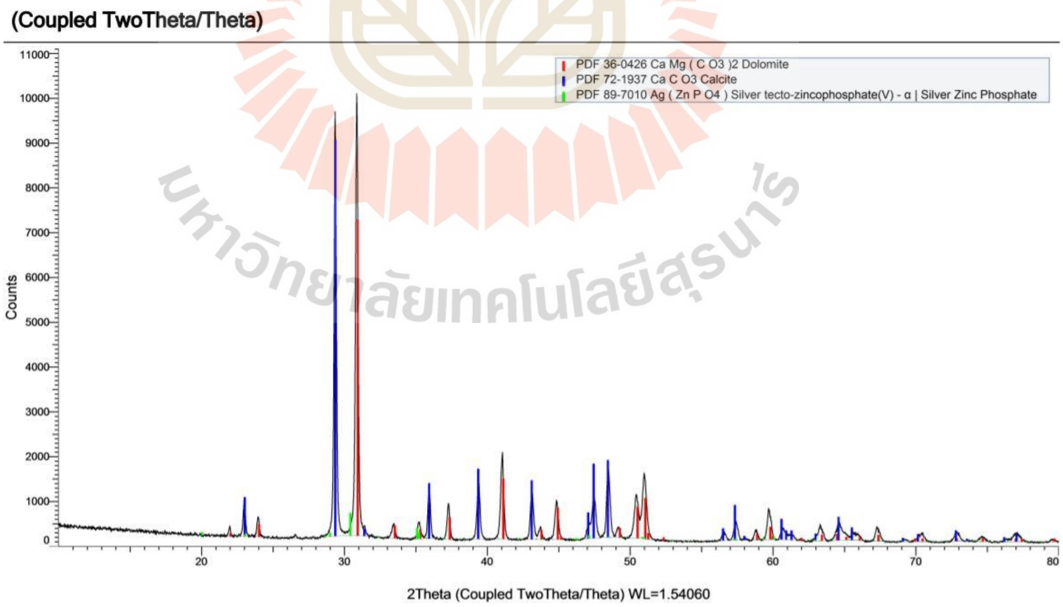

Figure A10. The graph shows the angle of theta which indicates the mineral that exists in the Nam Mahoran Formation after soaking with 5% HCl.

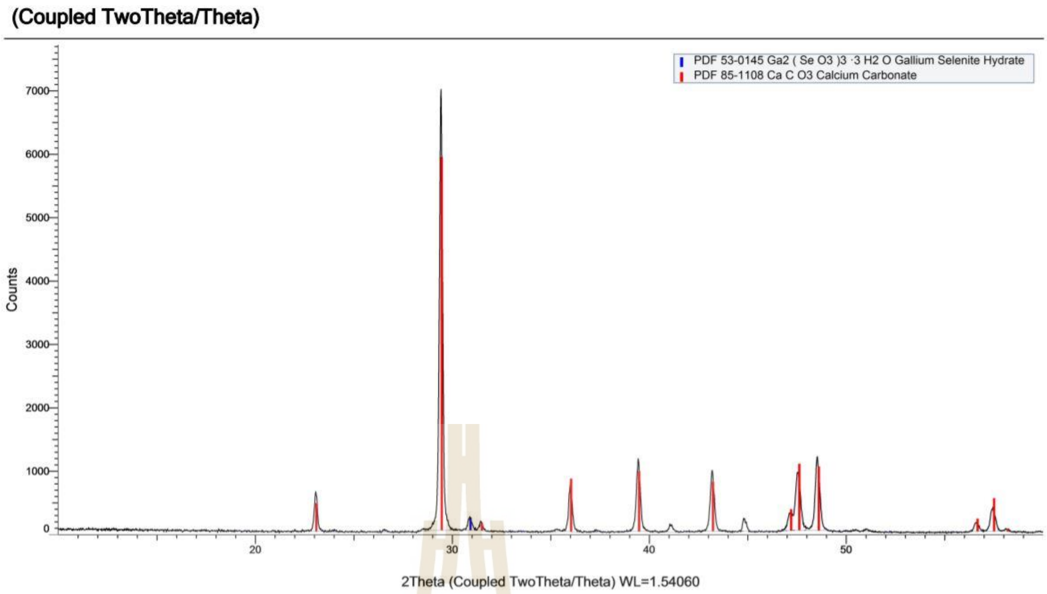

Figure A11. The graph shows the angle of theta which indicates the mineral that exists in the Nam Mahoran Formation after soaking with 10% HCl.

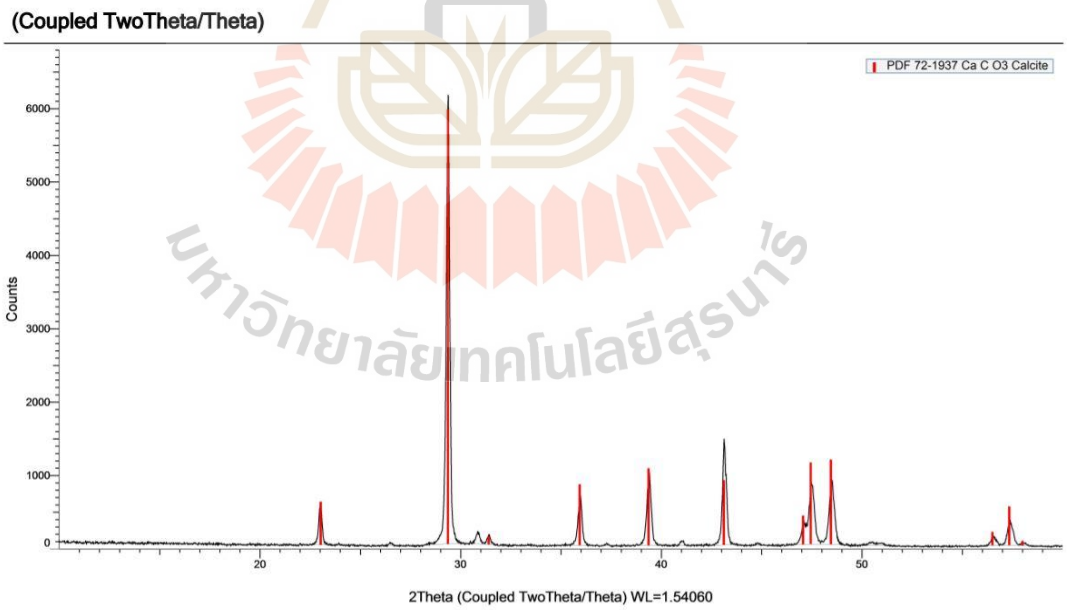

Figure A12. The graph shows the angle of theta which indicates the mineral that exists in the Nam Mahoran Formation after soaking with 15% HCl.

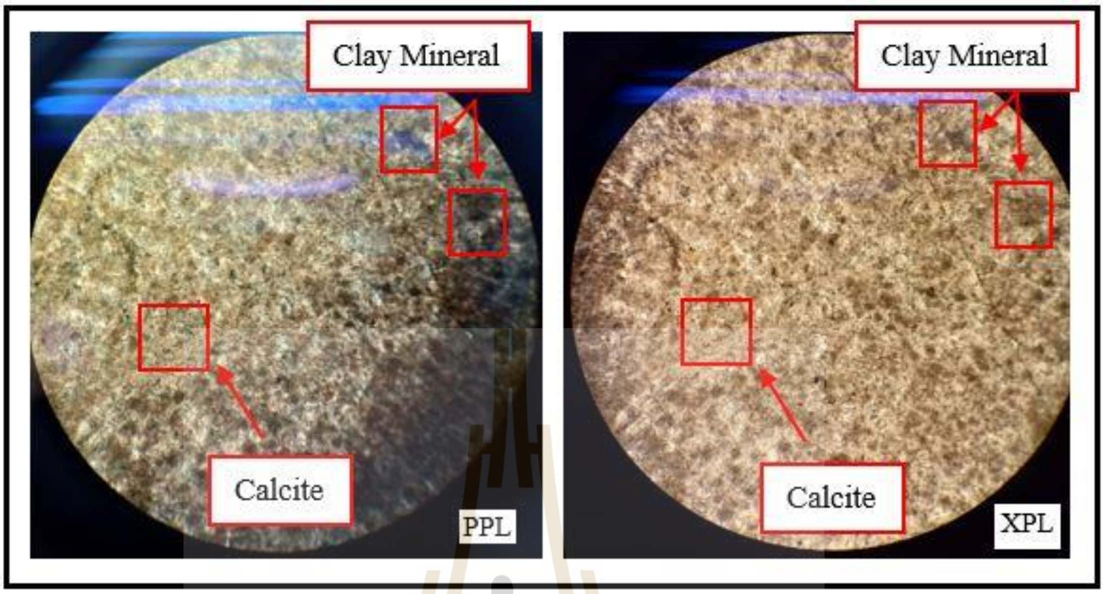

Figure A13 Petrography of thin section Pha Nok Khao formation.

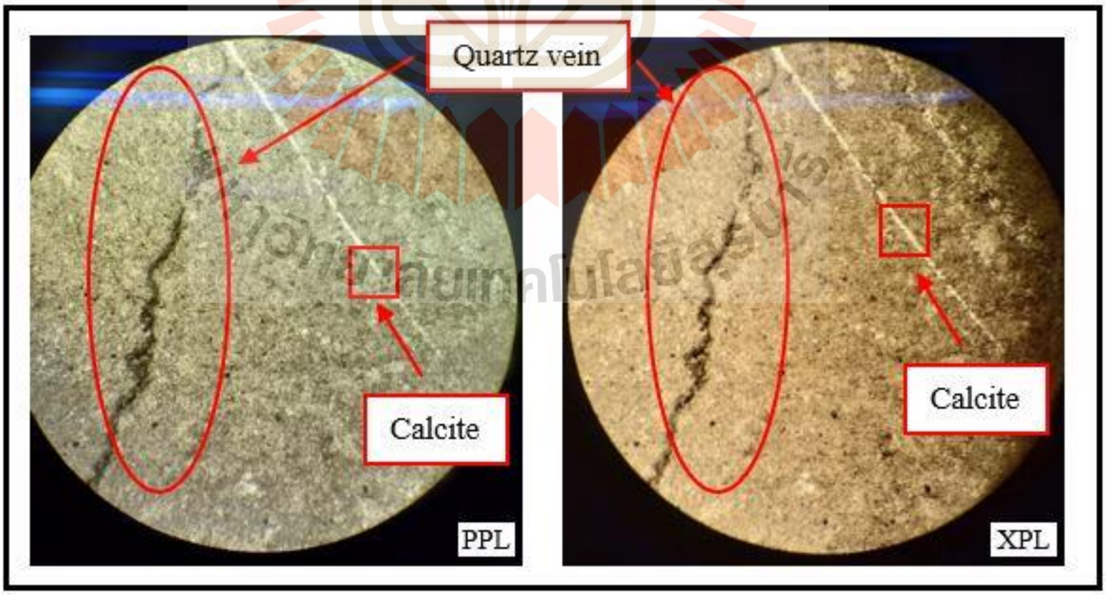

Figure A14 Petrography of thin section Nam Mahoran formation

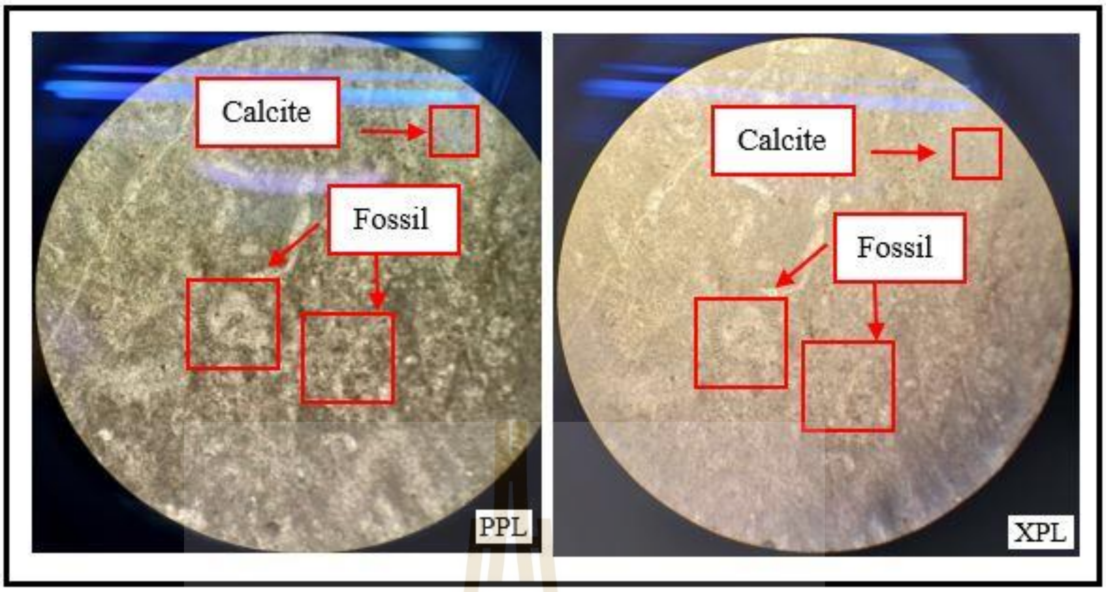

Figure A15 Petrography of thin section Khao Khad formation

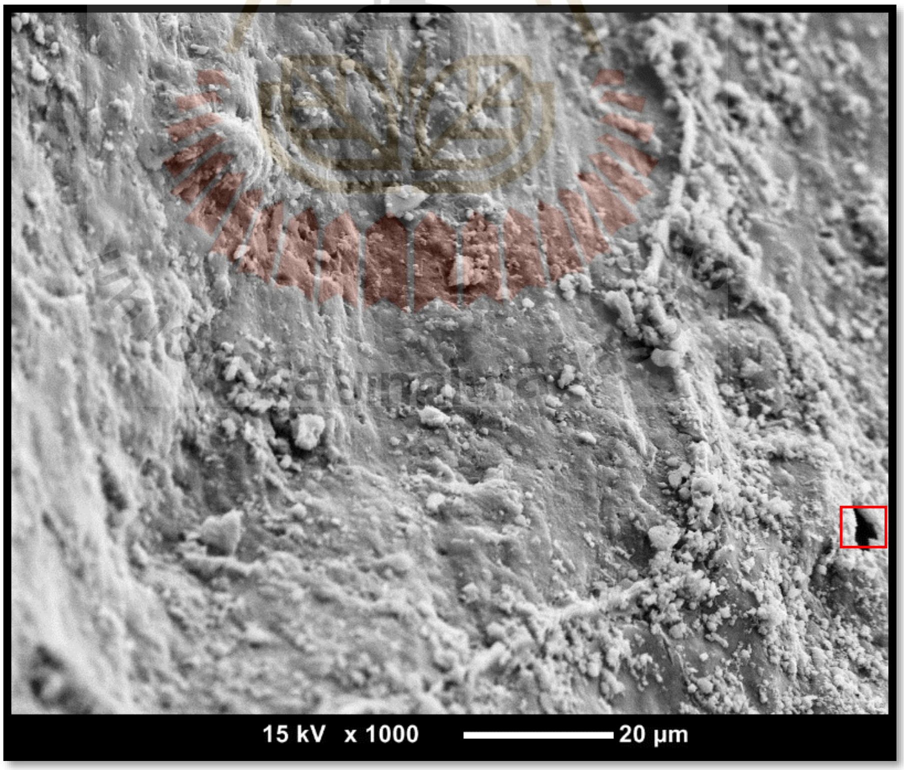

Figure A16 Morphology of Pha Nok Khao formation by SEM

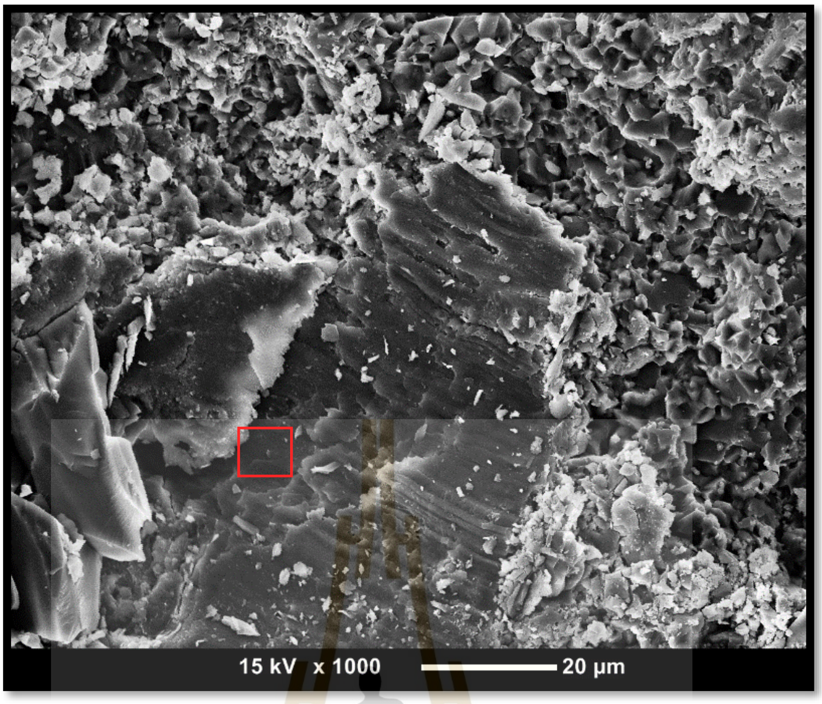

Figure A17 Morphology of Nam Mahoran formation by SEM

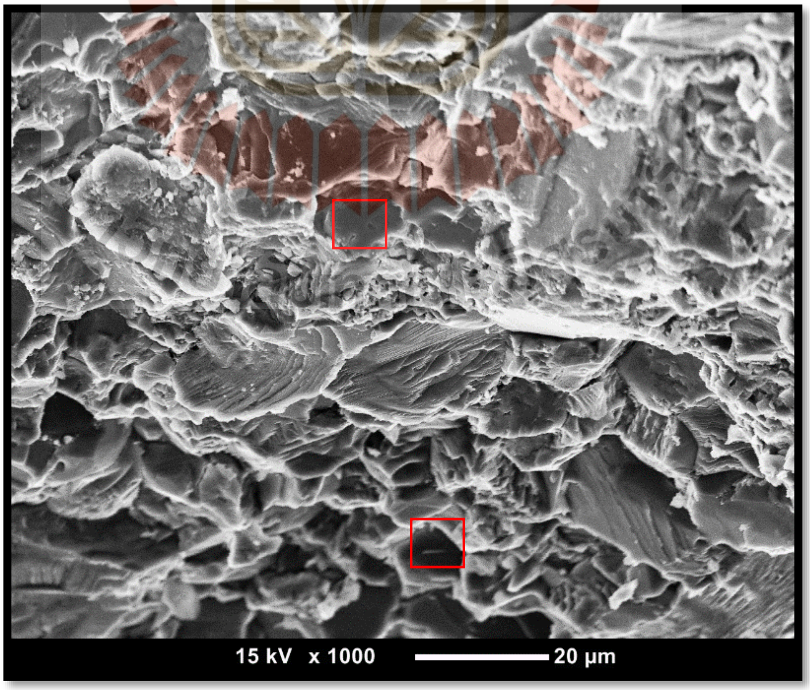

Figure A18 Morphology of Khao Khad formation by SEM

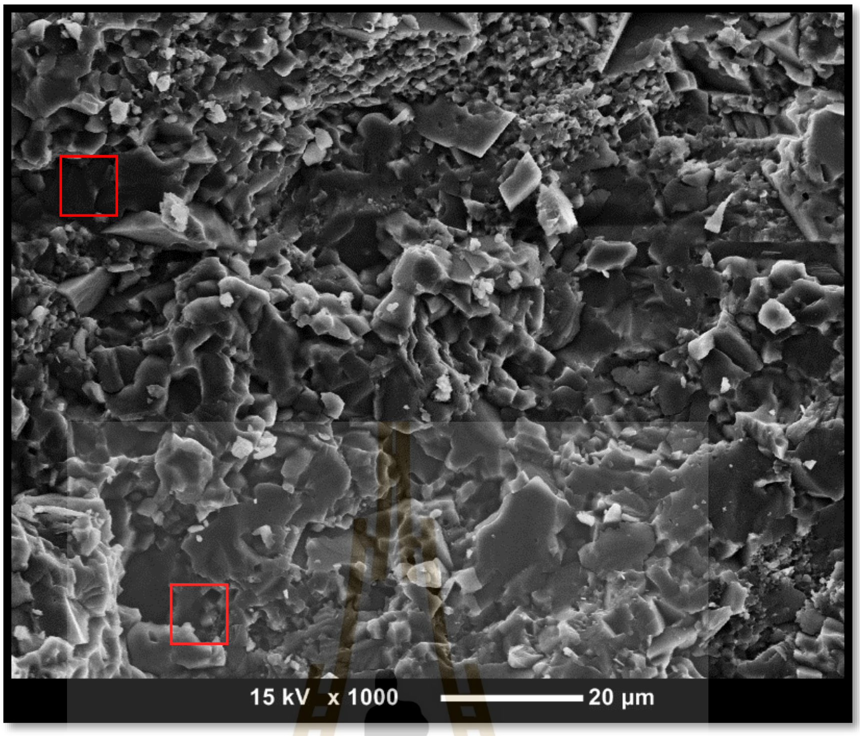

Figure A19 Morphology of Pha Nok Khao formation by SEM after soaked with 5 %

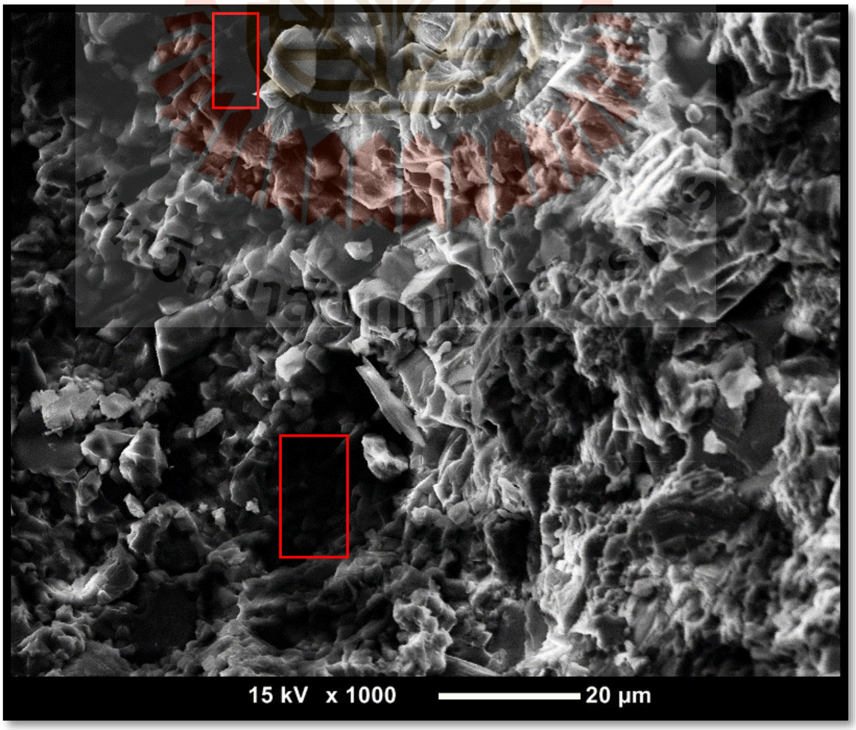

Figure A20 Morphology of Pha Nok Khao formation by SEM after soaked with 10 %

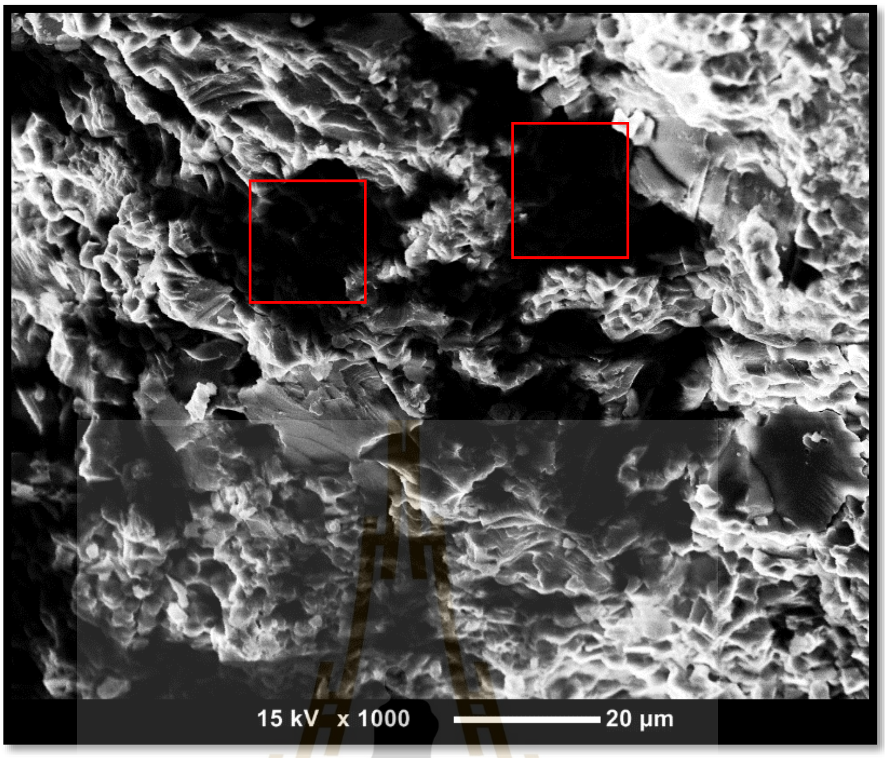

Figure A21 Morphology of Pha Nok Khao formation by SEM after soaked with 15 %

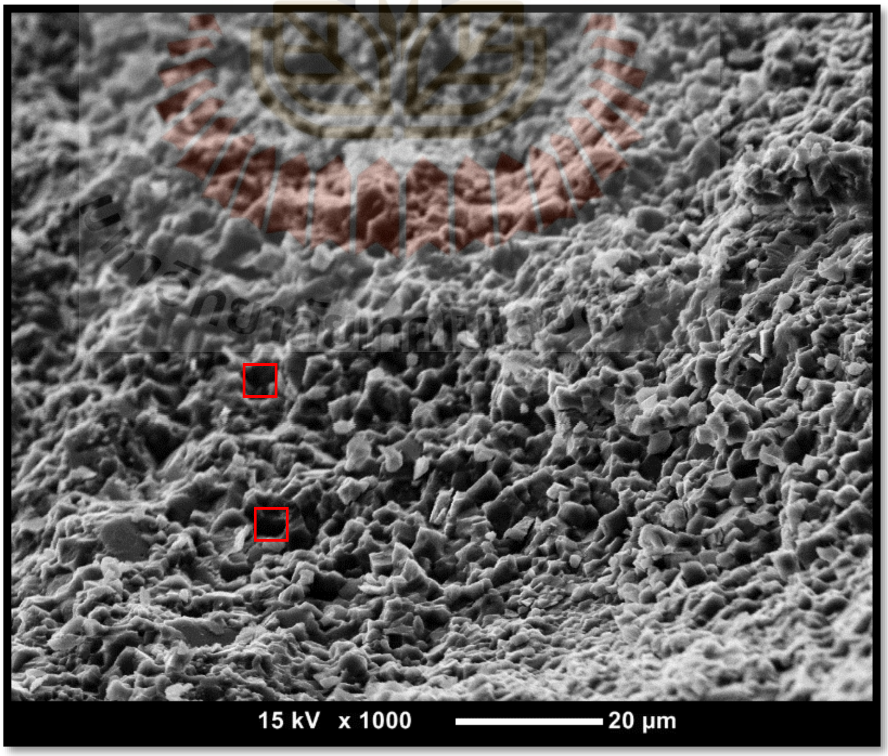

Figure A22 Morphology of Nam Mahoran formation by SEM after soaked with 5 %

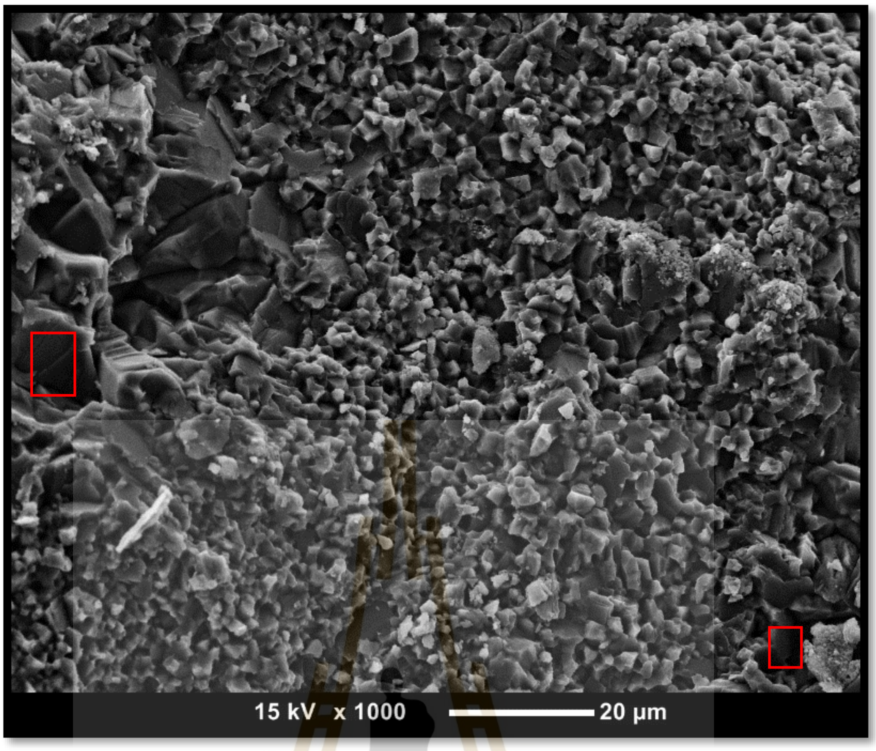

Figure A23 Morphology of Nam Mahoran formation by SEM after soaked with 10 %

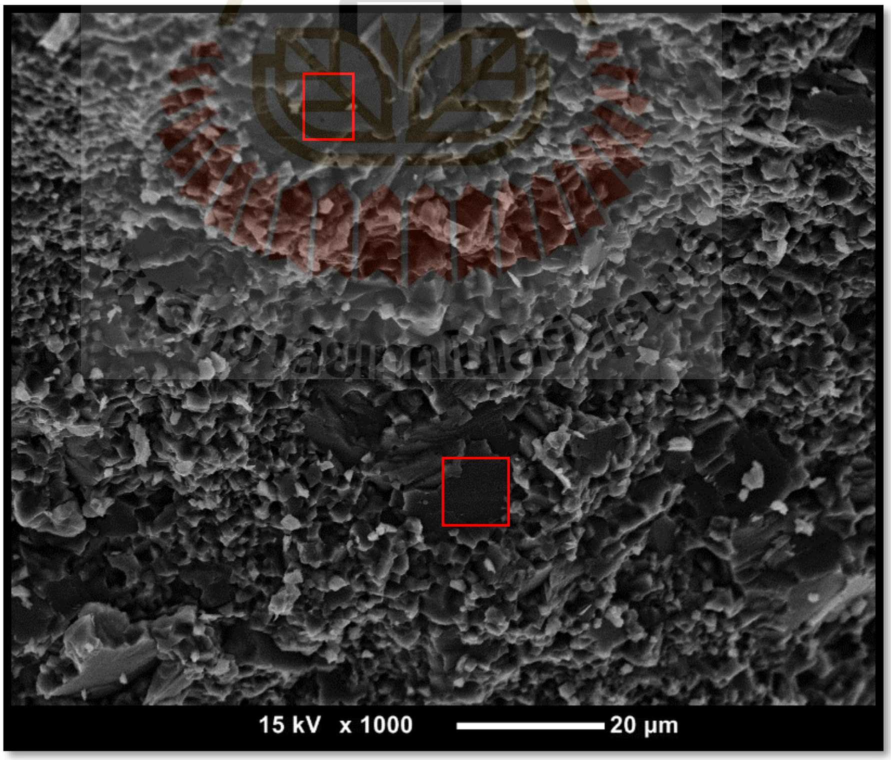

Figure A24 Morphology of Nam Mahoran formation by SEM after soaked with 15 %

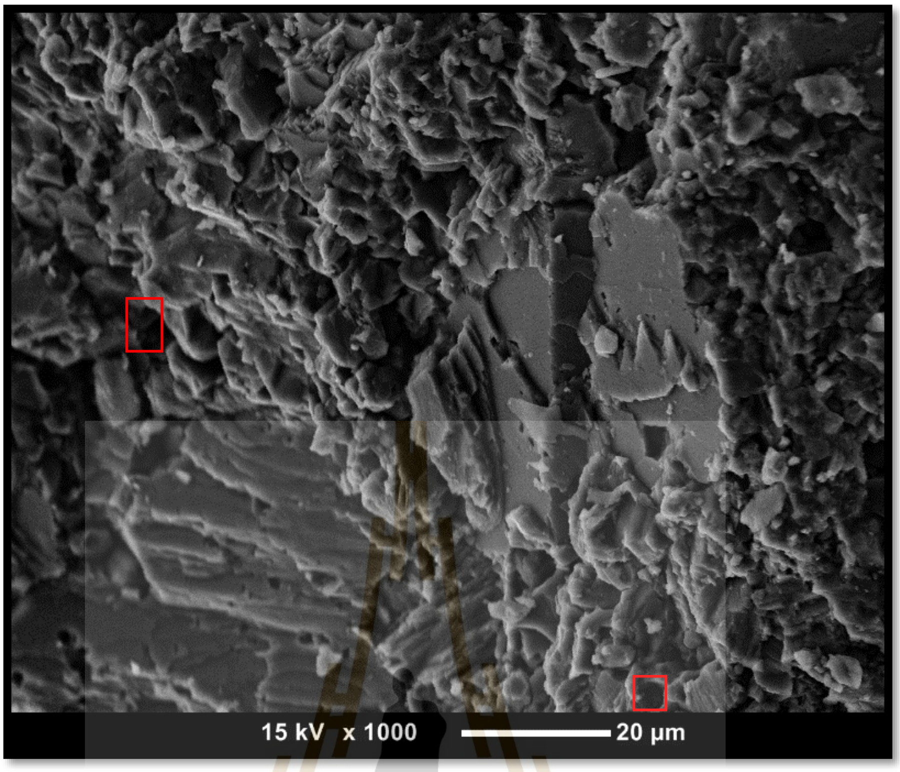

Figure A25 Morphology of Khao Khad formation by SEM after soaked with 5 %

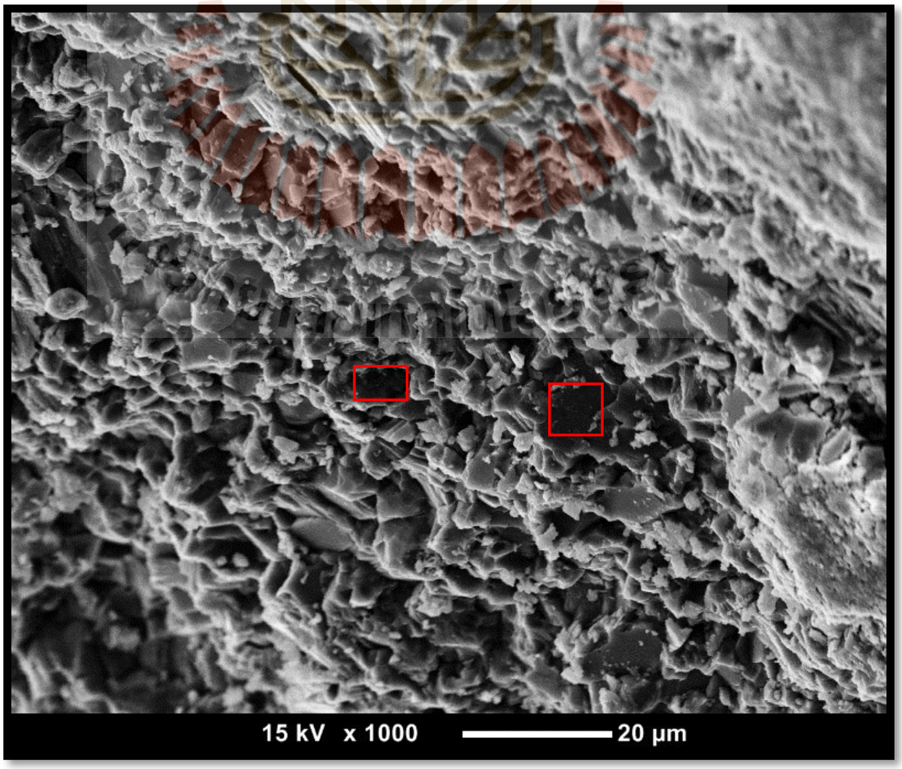

Figure A26 Morphology of Khao Khad formation by SEM after soaked with 10 %

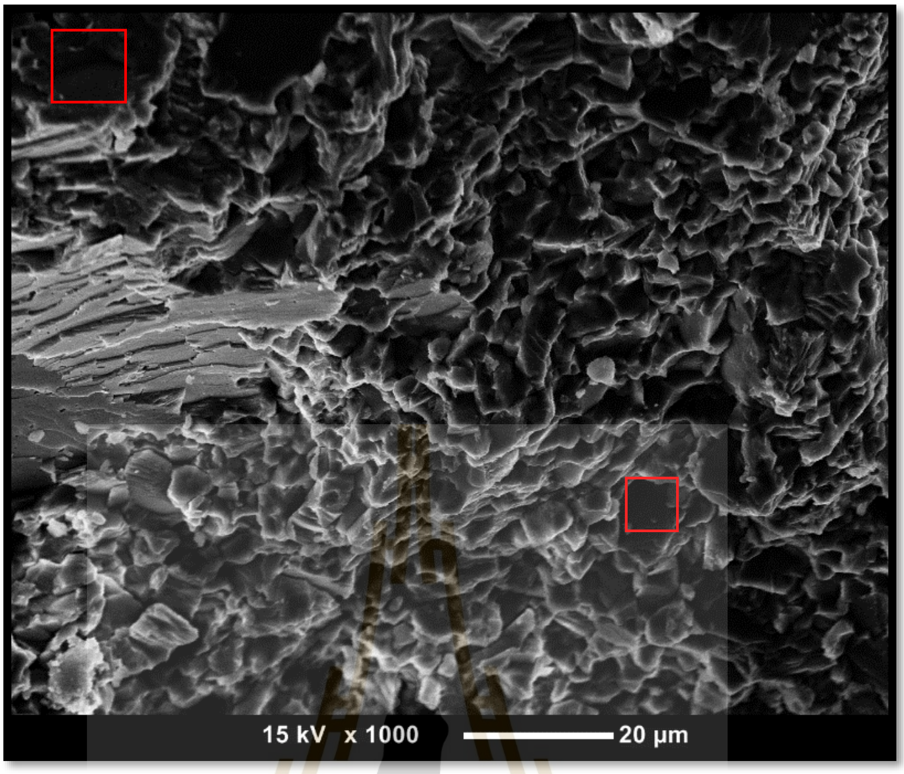

Figure A27 Morphology of Khao Khad formation by SEM after soaked with 15 %

BIOGRAPHY

Mr. Worachit Nakpong was born on April 29, 1995 in Bangkhla District, Chachoengsao Province, Thailand. In 2013, He began his bachelor's degree in Engineering (Geotechnology), Institute of Engineering at Suranaree University of Technology, Nakhon Ratchasima Province. After graduating bachelor's degree, he continued for a master's degree in the Geotechnology Program, Institute of Engineering, Suranaree university of Technology. During graduation, 2017-2019, he served in position of teacher and research assistant at SUT.