OPTIMIZATION OF PHYSICAL CHARACTERIZATION OF MALAYSIAN CLAY FOR CERAMIC TILE PRODUCTION

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OPTIMIZATION OF PHYSICAL CHARACTERIZATION OF MALAYSIAN CLAY FOR CERAMIC TILE PRODUCTION

by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AP	Apparent Porosity
BD	Bulk Density
CEC	Cation Exchange Capacity
CTE	Coefficient of Thermal Expansion
DF	Degree of Freedom
DTA	Differential Thermal Analysis
FSD	Fired Shrinkage in Diameter
FST	Fired Shrinkage in Thickness
MS	Mean Squares
PSD	Particle Size Distribution
R^2	Coefficient of Multiple Determination
R_A^2	Adjusted Coefficient of Multiple Determination
SEM	Scanning Electron Microscope
SG	Specific Gravity
SHMP	Sodium Hexametaphosphate
SMS	Sodium Metasilicate
SS	Sum of Squares
SSA	Specific Surface Area
StDev	Standard Deviation
STPP	Sodium Tripolyphosphate
TGA	Thermogravimetric Analysis
WA	Water Absorption

XRD	X – Ray Diffraction
XRF	X – Ray Fluorescence

PENGOPTIMUMAN CIRI-CIRI FIZIKAL TANAH LIAT MALAYSIA UNTUK PENGELUARAN JUBIN SERAMIK

ABSTRAK

Tanah liat merupakan bahan mentah penting dalam pembuatan jubin seramik. Dari segi ekonomi, lempung tempatan adalah penting untuk permintaan industri jubin seramik tempatan. Walau bagaimanapun, tiada kerja penyelidikan yang komprehensif dilakukan untuk lempung Malaysia untuk aplikasi dalam jubin seramik. Kerja penyelidikan ini bertujuan untuk menyediakan data saintifik mengenai ciri-ciri tanah liat Malaysia dari Ipoh (Perak), Kuala Rompin (Pahang) dan Mersing (Johor) dan kesesuaiannya untuk industri jubin seramik. Kajian ini merangkumi ciri-ciri tanah liat, kesan parameter pemprosesan jubin seramik untuk sifat-sifat tanah liat dan aplikasi dalam jubin seramik. Tanah liat yang dikaji dicirikan oleh komposisi kimia, analisis mineralogy, reologi, sifat fizikal, haba dan bakar. Keputusan menunjukkan bahawa tanah liat Ipoh adalah lebih kasar dengan saiz zarah (14.6 μm) berbanding dengan tanah liat Kuala Rompin (7.2 μm) dan Mersing (6.0 μm). Untuk reologi, sodium tripolifosfat (STPP) adalah deflocculant yang paling sesuai untuk mengkaji lempung dengan bacaan CEC 16 to 40 meq/100g dan optimum deflocculant 0.10 to 0.24% untuk pembuatan jubin seramik dengan proses penggilingan basah. Untuk analisis mineralogik, kaolinit hadir dengan banyak di tanah liat Ipoh kira-kira 78.7%, sementara Kuala Rompin dan lempung Mersing mengandungi peratusan tinggi kuarza (34.1% dan 43.9%) dan illite (39.1% dan 30.7%). Mineralogi tanah liat mempengaruhi sifat-sifat pembakaran tanah liat yang dikaji, di mana lempung Kuala Rompin dan Mersing menunjukkan kepadatan yang lebih tinggi (2.3 – 2.5 g/cm^3), pengecutan yang lebih tinggi (9.0 – 13.0%), penyerapan air yang lebih rendah (0.0 –

2.0%), CTE yang lebih tinggi (8.1 – 8.4 x10^{-6} °C^{-1}) dan warna yang lebih gelap (L* of 60 - 70) daripada tanah liat Ipoh pada suhu pembakaran 1200 °C. Untuk parameter pemprosesan, tekanan dan suhu pembakaran mempunyai kesan yang lebih besar kepada sifat-sifat pengeringan dan pembakaran, sementara kedua-dua pelembapan dan masa penggilingan mempunyai kesan kecil pada kedua-dua sifat pengeringan dan pembakaran lempung yang dipelajari. Reka bentuk statistik percubaan campuran membuktikan bahawa tanah liat yang dipelajari sesuai digunakan untuk pengeluaran jubin seramik tetapi aplikasinya sangat bergantung kepada amalan pengeluaran jubin seramik dengan tekanan dan suhu pembakaran. Untuk amalan pengeluaran komersial jubin lantai, tanah liat yang dikajian hanya memenuhi kategori jubin seramik BII_b dan BIII. Untuk amalan pengeluaran komersil jubin porselin, tanah liat yang dikajian telah memenuhi hampir semua kategori jubin seramik dari BI_a ke BIII. Hasil kerja penyelidikan menunjukkan bahawa mineralogi dan saiz zarah tanah liat, tekanan dan suhu pembakaran secara langsung mempengaruhi sifat bakar tanah liat yang dipelajari dan perumusan badan jubin seramik.

OPTIMIZATION OF PHYSICAL CHARACTERIZATION OF MALAYSIAN CLAY FOR CERAMIC TILE PRODUCTION

ABSTRACT

Clay is an important raw material in manufacturing of ceramic tiles. From economical point of view, local clays are important for demand of local ceramic tile industries. However, no comprehensive research work was carried out on Malaysia clays for application in ceramic tiles. The research work is aimed to provide scientific data on characterization of Malaysian clays from Ipoh (Perak), Kuala Rompin (Pahang) and Mersing (Johor) and their suitability for ceramic tile industry. The research covered characterization of study clays, effect of ceramic tile processing parameters on properties of studied clays and application in ceramic tiles. The clays were characterized by chemical composition, mineralogy, rheological analysis, physical, thermal and fired properties. Results showed that Ipoh clay is coarser in particle size (14.6 μm) than Kuala Rompin (7.2 μm) and Mersing clays (6.0 μm). For rheological behaviour, sodium tripolyphosphate (STPP) is the most suitable deflocculant for the studied clays with CEC of 16 to 40 meq/100g and optimum deflocculant of 0.10 to 0.24% for manufacturing of ceramic tiles by wet milling process. For mineralogical analysis, kaolinite was present abundantly in Ipoh clay of about 78.7%, while Kuala Rompin and Mersing clays are containing high percentage of quartz (34.1% and 43.9%, respectively) and illite (39.1% and 30.7%, respectively). Mineralogy of clay is greatly affecting the fired properties of studied clays, where Kuala Rompin and Mersing clays shown higher densification (2.3 – 2.5 g/cm^3), higher shrinkage (9.0 – 13.0%), lower water absorption (0.0 – 2.0%), higher CTE (8.1 – 8.4 $x10^{-6}$ $°C^{-1}$) and darker fired colour (L* of 60 - 70) than Ipoh clay at

firing temperature of 1200 °C. For processing parameters, pressing pressure and firing temperature have greater impact to drying and fired properties, while both moisturizing and milling time have minor effect on both drying and fired properties of studied clays. Statistical design of mixture experiment proves that the clays are suitable to be used for production of ceramic tiles but its application is highly dependent to ceramic tile production practice by pressing pressure and firing temperature. For commercial floor tile production practice, studied clays have only fulfilled categories of BII_b and BIII ceramic tiles. For commercial porcelain tile production practice, studied clays have fulfilled almost all the ranges of ceramic tiles from BI_a to BIII. The outcome of the research work shows that mineralogy and particle size of clay, pressing pressure and firing temperature have direct influenced on fired properties of studied clays and ceramic tiles body formulation.

CHAPTER ONE
INTRODUCTION

1.1 Introduction

The ceramic industry in Malaysia consists of variety of products that ranging from low-grade products (such as brick) to high-grade products (such as electronic ceramic materials). According to survey done by Minerals and Geoscience Department Malaysia, ceramic products are classified into five categories namely, structural clay products, household products, pottery, advanced ceramics components and formers (Hussin et al., 2013, Rosni et al., 2016).

Table 1.1 shows the survey of production value of various types of ceramics products according to five categories from year 2014 to 2016. According to the survey, the total production value of ceramic products has reduced by 21.4% from RM3,628.70 million in 2014 to RM2,851.52 million in 2016. In terms of products group, structural clay products have recorded the highest production value, which also indicates the important of ceramic products in Malaysia. Among all the ceramic products, wall/floor/mosaic & terracotta tiles have recorded the highest production values and follow by clay bricks. Tiles (such as wall, floor and porcelain tiles) are important products in Malaysia as its application are covered mostly to construction work for both residential and non-residential.

Malaysia has exported ceramic products to many countries with value of RM861.20 million in 2014, RM860.10 million in 2015 and RM810.98 million in 2016 (Rosni et al, 2016). The exported value is mainly referred to clay & refractory construction materials and pottery. For clay & refractory construction materials, major export destinations are Singapore, Australia, Thailand, Taiwan, Vietnam and others with export values of RM577.99 million in year 2016. For pottery, major export destinations are USA, Indonesia, Egypt, Australia, Russia and others with export value of RM232.99 million in year 2016.

Table 1.1: Production value of ceramic products components, 2014 – 2016 (Rosni et al., 2016)

Products Group	**Product Component**	**2014**	**2015**	**2016**
			RM Millions	
Structural Clay Products	Clay brick	657.68	582.24	554.83
	Clay pipes/sewage pipes/drain tiles	99.35	68.02	81.70
	Wall/floor/mosaic & terracotta tiles	1,937.12	1,709.79	1,436.69
	Clay roofing tiles	207.45	156.73	283.35
	Refractory bricks	71.77	45.09	48.66
	Subtotal	2,973.37	2,561.88	2,094.44
Household Ceramic Products	Ceramic tableware/porcelain	101.02	96.77	84.48
	Sanitary ware	195.18	213.01	211.85
	Subtotal	296.20	309.78	296.32
Pottery Products	Flower pot/decorative ware	115.68	137.19	141.98
	Cooking pot/stove	0.39	0.40	0.43
	Not classified	0.52	0.52	0.01
	Subtotal	116.59	138.08	142.42
Advance Ceramic Component	Electronic component products	156.71	167.39	178.19
	Ceramic fibre/ceramic insulators	14.60	14.18	27.59
	Ceramic powder	13.50	13.50	17.28
	Subtotal	184.81	195.07	223.06
Formers	Ceramic formers	57.73	70.05	95.27
	Subtotal	57.73	70.05	95.27
	Total	3,628.70	3,274.86	2,851.52

On the other hand, Malaysia has imported clay & refractory construction materials and pottery from many countries with imported value of RM787.16 million in 2014, RM954.51 million in 2015 and RM1.076.14 million in 2016 (Rosni et al., 2016). Clay & refractory construction materials were imported from China, Vietnam, Thailand, Indonesia, India and Others with total values of RM900.82 million in 2016. For pottery, it was imported from China, Thailand, Indonesia, Japan, Vietnam and Others with values of RM175.32 million in 2016. Therefore, both clay & refractory construction materials and pottery were considered important to the growth of Malaysia economy.

1.2 General Geological Survey of Clay-Based Industry in Malaysia

The mining industry has contributed to the growth and development for economic of many countries. Malaysia is rich with various types of minerals especially clay. The total production of clay in Malaysia in year 2016 has recorded as 5.8 million tonnes with leading clay producing state from Johor (1,588,847 tonnes), followed by Sarawak (833,365 tonnes), Selangor (794,309 tonnes), Kedah (556,177 tonnes), Pahang (438,198 tonnes), Negeri Sembilan (423,750 tonnes), Sabah (399,857 tonnes), Perak (274,000 tonnes), Perlis (225,891 tonnes), Melaka (126,450 tonnes), Penang (87,450 tonnes) and Kelantan (20,124 tonnes) (Iszaynuddin et al., 2016). In Malaysia, the mining of clay is fall into the category of non-metallic minerals.

According to report from Mintrade 2016 (Nightingale et al., 2016), clay and other clays minerals from Malaysia were exported to many countries. Table 1.2 shows the exports of clay and other clays minerals by major countries. Overall, export on clay and other clays minerals were reduced from 362,837 tonnes in 2014 to 320,918 tonnes in 2016 by 11.6%. Bangladesh was the major buyer on clay and other clays minerals from Malaysia and follow by Indonesia and UAE. Generally, report from Mintrade 2016 shows the increasing demands on Malaysia's clay and other clays minerals by Bangladesh from year 2014 to 2016. Bangladesh was reported with increase of 19.5% (by quantity in tonnes) from year 2014 to 2016. However, Indonesia, UAE, Taiwan, India, Thailand and others were reported with reduction of export of clay and other clays minerals from Malaysia from year 2014 to 2016. The export market of clay and other clays minerals has showed the important of minerals in Malaysia to ceramic industries in other countries as total demand is considered high in quantity.

Table 1.2: Export of Malaysian clay and other clays minerals by various countries (Nightingale et al., 2016)

	Year 2014		**Year 2015**		**Year 2016**	
Country	**Quantity (Tonnes)**	**Value (RM)**	**Quantity (Tonnes)**	**Value (RM)**	**Quantity (Tonnes)**	**Value (RM)**
Bangladesh	200,059	23,995,766	212,351	16,395,190	239,019	30,361,339
Indonesia	34,371	19,788,902	39,268	25,368,069	19,361	17,521,771
UAE	85,569	4,833,160	59,453	3,818,189	45,281	5,147,247
Taiwan	20,299	1,301,938	13,344	1,419,697	12,176	1,900,489
India	8,500	137,450	3,554	163,272	4,055	689,474
Thailand	989	545,291	964	491,254	274	99,563
Others	13,050	1,136,297	1,092	712,025	752	276,928
Total	**362,837**	**51,738,804**	**330,026**	**48,367,696**	**320,918**	**55,996,811**

Malaysia also imports clay and other clays minerals from other countries. According to report from Mintrade 2016 (Nightingale et al., 2016), clay and other clays minerals were imported from many countries. Table 1.3 shows the import of clay and other clays minerals from major countries. China was the major exported clay and other clays minerals to Malaysia and followed by Thailand, Japan, India, Taiwan, USA and others. Overall, the total import of clay and other clays minerals from other countries were reduced by 77.2% from 14,346 tonnes in 2014 to 3,267 in year 2016. Mintrade 2016 has reported the reduction of imported clay and other clays minerals from China, Taiwan and USA from year 2014 to 2016. The increase in imported clay and other clays minerals from Thailand, Japan and India was reported as 18.0%, 52.6% and 362.0%, respectively. The reduction in imported clay and other clays minerals is probably due to replacement by local minerals to reduce total cost of raw materials as compare with overseas minerals due to high transportation cost.

Table 1.3: Import of clay and other clays minerals from various countries (Nightingale et al., 2016)

Country	Year 2014		Year 2015		Year 2016	
	Quantity (Tonnes)	**Value (RM)**	**Quantity (Tonnes)**	**Value (RM)**	**Quantity (Tonnes)**	**Value (RM)**
China	23,537	37,555,073	19,765	40,022,167	15,975	21,237,698
Thailand	15,359	11,153,416	19,546	16,269,426	18,124	15,539,514
Japan	1,256	2,251,501	1,772	2,941,349	1,917	3,552,446
India	1,604	4,078,893	7,569	2,342,228	7,409	2,363,744
Taiwan	1,493	2,685,006	489	967,369	1,068	2,110,857
USA	1,426	2,228,505	491	1,303,592	960	1,945,321
Others	14,346	5,404,994	4,780	6,812,820	3,267	6,062,722
Total	**59,021**	**65,357,388**	**54,412**	**70,658,951**	**48,720**	**52,812,302**

1.3 Problem Statement

From economical point of view, local clay deposits are considered most important to fulfil the demand of both local and oversea ceramic industries. Although clay is a primary raw material for local ceramic industries, however, no comprehensive research work was carried out on clay in Malaysia to clearly characterized in details on its potential and properties in application to ceramic tiles, such as physical properties, mineralogical properties, chemical composition, thermal behaviour, firing properties and rheological properties.

The knowledge of the characteristics and properties of clay in Malaysia are essential especially in application, designing and developing ceramic body formulation for ceramic tiles industry. The research study on local minerals is crucial as it is not only able to fulfil local demands especially related to ceramic industries but also able to expand the application of that minerals in different area or field that eventually will be able to fulfil the needs or requirement in many booming industries and perhaps in developing advance technologies.

However, limited research works were conducted on clays in Malaysia in relation to ceramic tile as most research works related with clays were only carried out and reported by Minerals and Geoscience Department Malaysia. Furthermore, their reports not very focus for specific application especially for production of ceramic tile. Knowledge of clays is essential in application. Designing and developing ceramic tile body formulation. Also, not many research works focussed on the traditional ceramics in Malaysia as most researchers focus on research work related to advanced ceramic materials.

The research work on the characteristics of clay and application in ceramic tile industries will be mainly focused on the clay from the area of Mersing (Johor), Ipoh (Perak) and Kuala Rompin (Pahang) due to its abundant in clay reserve and strategic location for ceramic industries such as ceramic tile manufacturer in Malaysia, especially in the state of Perak, Johor, Selangor and Negeri Sembilan. The research work is important and is useful to expand and optimize the application in ceramic tile industries and might be as well as open up new areas of application. For this reason, attention of Malaysia clay should be paid by investigation or research approach, which eventually can provide benefit to both academic and commercial industries.

1.4 Objective of the Research Work

The research works on clay in Malaysia is needed as it is important to fulfil the needs from local industries (especially ceramic tile manufacturers) and perhaps in developing potential market related to advanced technology. The following shows the objectives of this research work:

a. To examine the behaviour and characteristics of studied clays in physical and thermal properties together with mineralogy, chemical composition, rheological, unfired and fired properties.

b. To determine the effect of ceramic tile manufacturing processing parameters against physical and fired properties of studied clays. To optimize the application of studied clays in application of ceramic tile.

c. To appraise the potential and suitability of studied clays in development of ceramic tiles body formulation and its application and contribution to manufacturing of ceramic tile.

1.5 Scope of the Research Work

Research work was designed step by step to cover most areas and scopes of research of clays from behaviour and properties of studied clays to application in manufacturing of ceramic tile to achieve the above mentioned objectives. The research work has divided into four parts:

Part 1: To characterize the Malaysia bulk clays (natural state or unprocessed clay) on their chemical composition, mineralogical, physical, thermal and rheological properties. The studied clays were also fired at 1000 °C, 1100 °C and 1200 °C to characterize and compare with their mineralogy and morphology in both raw clay and fired formed. Furthermore, mineralogical property of studied clay in clay fraction was also determined for comparison between natural and treated formed of studied clays.

Part 2: To explore and investigate the role of moisture content of powder during moisturizing process and pressing pressure on their drying and fired properties of studied clays. To determine the properties, the studied clays were introduced with moisture content ranging from 4 – 10% and pressing pressure ranging from 15 – 36 MPa, which subsequently fired at 1200 °C.

Part 3: To investigate the effect of milling time and firing temperature of studied clays on physical, drying and fired properties. The drying properties were analysed by one-way analysis of variance (ANOVA) test to determine the effect of the factor on the data obtained by the determination of the significant differences of the milling time and comparative analysis of the mean values of drying shrinkage. The effect of milling time and firing temperature on fired properties of studied clays were evaluated by multi-variable chart and follow by prediction of ceramic tiles from properties of studied clays

Part 4: To characterize the fired properties of ceramic tiles body formulation (studied clays + commercial feldspar + commercial silica). In this part, ten mixture of body formulation design by using statistical design of mixture experiments (Minitab 16) were prepared according to

(A) Common commercial floor tile production practice with pressing pressure of 20 MPa and firing temperature of 1105 °C.

(B) Common commercial porcelain tile production practice with pressing pressure of 31 MPa and firing temperature of 1170 °C.

The analysis from statistical design of mixture experiments was used to optimize the suitable mixtures according to standard desired ceramic tile properties by classification of ceramic tiles with respect to ISO 13006, 2012.

CHAPTER TWO
LITERATURE REVIEWS

2.1 Introduction

Clay is the oldest ceramic raw materials. Clay is a natural occurring, earthy and fine grained material, which develops plasticity when mixed with water and will harden with dried or fired (Grim, 1968; Guggenheim & Martin, 1995). Clay has been well known and used by human being ever since the ancient time (Grim, 1968). Clay can be found easily everywhere but differs in purity. Clay is a basic raw material in manufacturing of traditional ceramics products such as floor tiles, wall tiles, porcelain tiles, roofing tiles, clay pipes, sanitary wares, bricks, refractories and kitchen wares.

Clay is used in ceramic tile as a source of silica and alumina, provide plasticity and mechanical strength, which is important in moulding, pressing processes and fired properties of ceramic tiles. Clay is an important raw material in producing ceramic tiles. So far, it is impossible to produce ceramic tile without using any clay. Generally, clay used by ceramic tile manufacturer was supplied in the raw form without prior processing such as shredding and blending, which delivered straight from the clay mine without any processing. Clay is usually exists as a mixture of different types of minerals together with traces of metal oxides and organic matter. Many types of clay mineral can be found in Malaysia (Abdullah et al., 2013) such as kaolinite, montmorillonite, muscovite and illite. The properties and characteristics of clays are derived from these clay minerals.

For ceramic tile manufacturing with wet milling process, it is always desired to obtain slip with high solid content with low viscosity, which is important for subsequent spray drying process of slip to ensure low energy consumption to evaporate water during atomization process in formation of spray powders granules. Furthermore, the production of clay-based ceramic products is always involved with thermal reaction, vitrification and sintering processes. Thermal analysis has become a powerful tool to understand the reaction of clay against firing temperature. Therefore, it is crucial in selection of clay for ceramic tile manufacturer to meet the requirement in physical, rheological and fired properties.

In terms of supply of clay, tile manufacturer always encountered problems due to depletion of clay reserve that eventually lead to frequent reformulation in body formulation of ceramic tile, which will affect the stability of production of tiles. It is always desired to use clay with huge reserve and consistent quality of reserve to minimize variation. For cost effective reason in producing of ceramic tiles, local ceramic tiles manufacturer will always use raw materials from local supply instead of overseas to ensure the overall cost of manufacturing of ceramic tiles is competitive in both local and overseas markets.

For economical point of view, the demand for clay has growth steadily (Özkan et al., 2010). The production of ceramic tiles is growing worldwide and has already exceeded 10 billion m^2 in year 2012 (Dondi et al., 2014). The impressive growth of ceramic tiles industry has implied the great demand for raw materials, where global consumption is estimated at about 230 million tons per year. Clay was considered as one of the raw materials that greatly needed for ceramic tile manufacturer and its potential is still growing globally.

Clays from Ipoh (Perak), Kuala Rompin (Pahang) and Mersing (Johor) are very important to ceramic industry especially ceramic tile manufacturers due to their cost advantages in terms of distance and transportation cost. However, it is rather difficult to assess the data and research information on the studied clays as most Malaysia clays are not yet characterized and evaluated in details in terms of chemical composition, physical and thermal properties based on their mineralogy. These knowledges are very crucial for evaluation of suitability and application of studied clays as raw materials especially for ceramic tile manufacturers. Therefore, the research work will be mainly focussed on studied clays and its application to production of ceramic tiles.

2.2 Background and Geological Setting of Clay in Perak, Pahang and Johor

Figure 2.1 shows the location of clay pits, kaolin mines and mica mines in the state of Perak in Malaysia. Clay pits were found in many locations in Perak in the area of Sg. Siput, Chemor, Ipoh, Batu Gajah, Kuala Kangsar, Trong, Beruas, Tapah and Bidor. However, kaolin mines were found in Perak in the area of Gopeng, Tapah and Bidor. Cheang et al. (2013) has reported the kaolin and sand in the Tapah-Bidor area of the Kinta-valley in Perak, Malaysia. The kaolin in Kinta-valley is derived from the weathering of feldspar-rich rocks or granites, which can be of primary or secondary origin. Cheang et al. (2013) has also reported that primary kaolins are formed *in situ* from hydrothermal processes related to magmatic activities and have not undergone any major transportation, which recognised by several cross section quartz veins that are still intact (Ariffin et al., 2008). However, secondary kaolin deposits have been eroded, transported and deposited in rivers and lakes over a large area and on other bedrocks such as limestone and schist underlying the Kinta valley, together with layers of sand, silts, gravels, vegetation and rocks fragments, to form the tin placers of Malaysia. Cheang et al. (2013) has concluded that mineralogical analysis of clay from Tapah and Bidor is mainly consists of kaolinite, muscovite and quartz minerals with highly kaolinite content and low in free silica.

Figure 2.1: Location of clay pits, kaolin mines and mica mines in Perak (Marto et al., 2013)

The location of Perak state with borders of Kedah state and the Thailand Yala Province to the north; Penang state was to the northwest; Kelantan and Pahang state to the east; Selangor state to the south, and the Straits of Malacca to the west. Perak state has an area of 21,006 km^2 (Director of National Mapping Malaysia, 1989). Perak state is the second largest state in Peninsular, which comprises of 6.4% of the total land area of Malaysia. Perak state has a unique geological context which is located on The Main Granite Range of Peninsular Malaysia (Director of National Mapping Malaysia 1989). It is also a well-known state for tin mining (Omar et al., 2006). Perak state is divided into six major geological contexts that is Quaternary (mainly recent alluvium), Triassic-Jurassic (sedimentary rocks), Carboniferous (sedimentary rocks), Devonian (sedimentary rocks), Silurian (sedimentary rocks with associated lava and tuff), and acid undifferentiated (acid intrusive) which consist of igneous granite rock (Ramli et al., 2016).

Pahang is considered the largest state in the peninsular Malaysia and the third largest after Sarawak and Sabah. According to Department of Statistical Malaysia, Pahang covers an area of 36,137 km^2 with population of about 1.5 million and has 11 districts (Gabdo et al., 2016). The geology of Pahang State is characterized by eight underlying geological formations, namely Quaternary, Cretaceous–Jurassic, Triassic, Permian, Carboniferous, Devonian, Silurian–Ordovician and acid intrusive. The geological survey Department of Malaysia has carried out a reconnaissance survey of clay resources and its potential over a major zone in central and south eastern Pahang during the fifth Malaysia Plan period (1986-1990) (Wan, 1996). According to the survey, clay deposit was found at Hulu Sungai Anak Endau in Kuala Rompin. The clay is the product of *in situ* residual decomposition of the coarse-grained granite and aplite. Sungai Anak Endau is generally low laying, swampy and surrounded by undulating hills. The low laying areas are generally covered with alluvium. The geology of these areas comprise of metasediment, granite and volcanic rocks (Sidek & Ong, 1993). Figure 2.2 shows the location of kaolin mines and sand pits in the state of Pahang, Malaysia. Generally, sand pits were found scattered across Pahang, while kaolin mine was located mainly in the area near to Kuala Rompin, Pahang near to the border between the state of Pahang and Johor. Therefore, clay from Kuala

Rompin was selected in this research work to evaluate its potential in ceramic tile manufacturing.

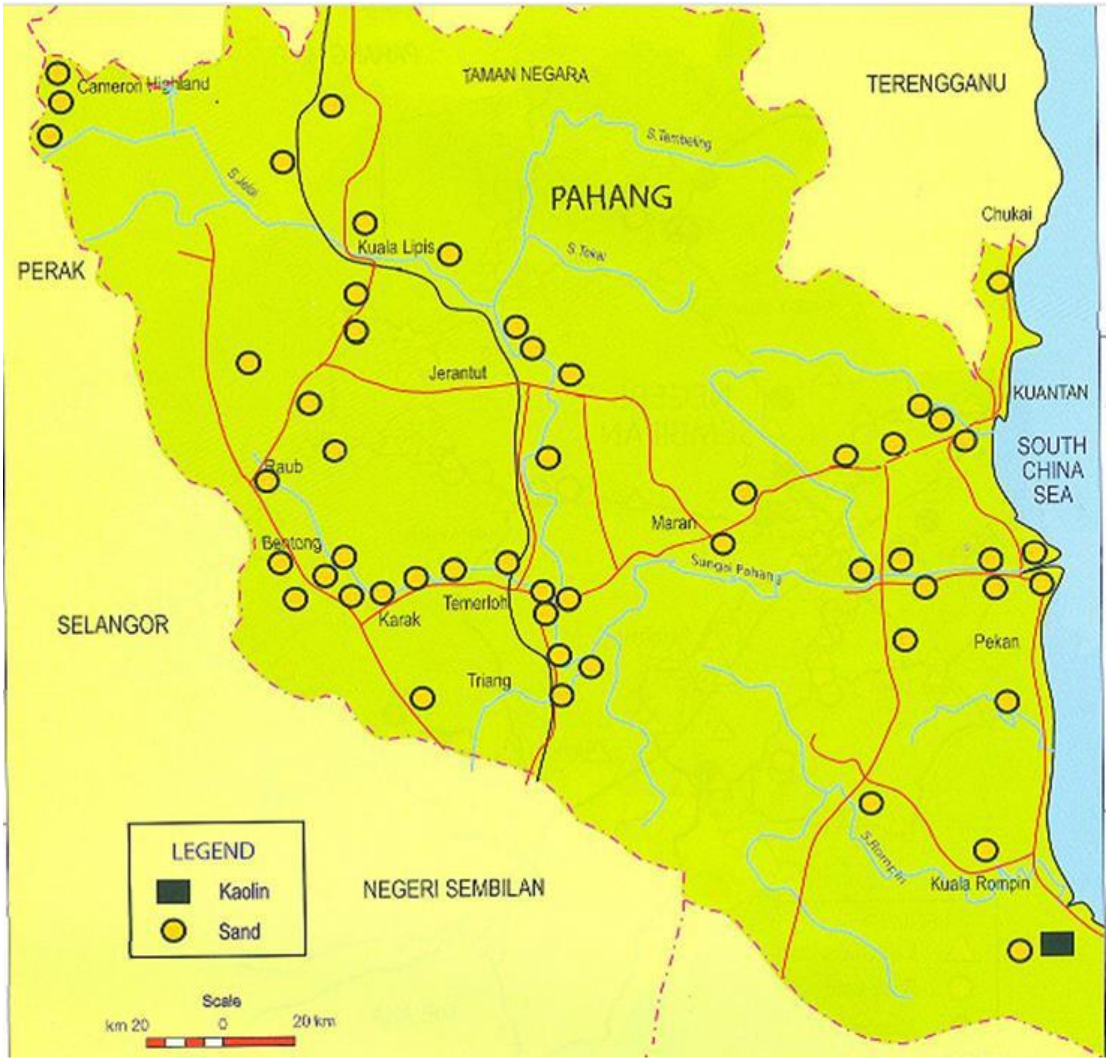

Figure 2.2: Location of kaolin mines and sand pits in Pahang (Marto et al., 2013)

Figure 2.3 shows the location of kaolin mine, iron ore mine, bauxite mine, tin mine and silica sand mine in Johor. Johor state is considered the fifth largest state in Malaysia. Johor is situated in the southern part of Peninsular Malaysia. It shares borders with Malacca and Negeri Sembilan states to the Northwest, Pahang state to the North, South China Sea to the East, Malacca straits to the West and the Republic of Singapore to the south with a tropical climate. Most of the land in Johor is utilized for agriculture, mainly oil palm and rubber plantations, which it covers a total land area of 19,210 km^2 and population of about 3.2 million as of 2010 (Saleh et al., 2015). For geological survey, Johor has six main geological formations underlying the soil, namely Quaternary, Tertiary, Cretaceous-Jurassic, Triassic, Permian, Intermediate Intrusive, Acid Intrusive and Devonian. The soils of Johor can be classified according to their parent material into three broad groups, namely sedimentary, alluvial and miscellaneous soils. On the basis of similar characteristics, of which the parent material is the most important, these soils have been differentiated into soil series and associations. The distribution pattern of these soil series and associations reveals a close relation with those of different geological lithologies within the state (Saleh et al., 2015).

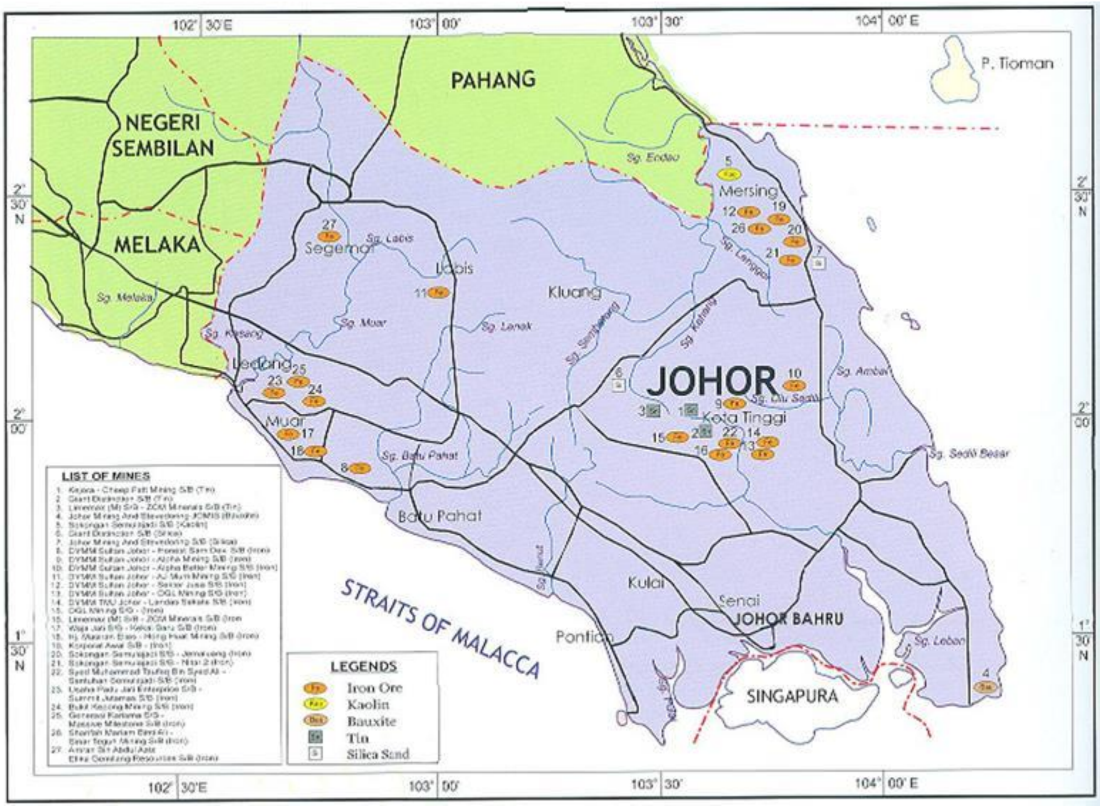

Figure 2.3: Mine location map in Johor (Majid et al., 2013)

Johor is rich with minerals that are suitable for ceramic industries. Abdullah and Aziz (2013) has reported that most minerals in Johor are deposited at east of Johor, especially Mersing, Murau Dohol, Linggiu, Sedili, Pengerang and Tanjung Leman. Zainol & Hasan (2000) have reported that Mersing is rich with kaolin with estimated reserve of 4.86 million metric ton, which is considered one of the important sources of clay for tile manufacturer. Furthermore, the latest geological survey of state of Johor also reported that kaolin mine is mainly located in the area of Mersing, Johor (Husin & Hasan, 2000; Majid et al., 2013). The study of clay from Mersing, Johor is crucial to understand its characteristics and applications in ceramic industries such as tile manufacturer.

2.3 Clay and Clay Minerals

2.3.1 Introduction of Clay

Clay is considered one of the oldest ceramic raw materials. Clay was referred as earthy materials that consists of minerals that rich in silica, alumina and water. Clay is widely used in manufacturing of ceramic products as raw materials, such as ceramic tiles, clay pipes, bricks, table wares, sanitary wares, refractories and decorative wares. Clay can be found easily everywhere but differs in purity. Generally, the demand for clay in the ceramic industry has grown steadily with the selection of clay was done in the perspective of quality and low transportation cost (Özkan et al., 2010). Therefore, ceramic industry has to use clays deposit from nearby area for economic reasons (Seli et al., 2013). As a consequence, the characteristics of clay especially from Ipoh, Kuala Rompin and Mersing are important for the technical performance of ceramic products (Ouahabi et al., 2014).

For tile manufacturers, clay is one of the most important raw materials. It is impossible to produce ceramic tiles without using any clay. Generally, most of the clay used by tile manufacturers is supplied in the raw form without prior processing such as shredding and blending. This is especially true for tile manufacturer as clays used are basically in the raw form straight from the mine. In addition, the use of clays for ceramic tiles and their commercial classification is depending on the technological and appearance requirements of ceramic bodies, such as fired colour (Dondi et al., 2014). Furthermore, the development of ceramic tiles body formulation are depending to properties of clay such as fusibility, rheological, drying and fired properties, which in most cases highly depending to clay's mineralogy, chemical composition and particle size distribution.

2.3.2 Definition and Characteristics of Clay and Clay Minerals

Clay is a natural occurring, earthly and fine grained material, which develops plasticity when mixed with an appropriate amount of water and will harden with dried or fired (Grim, 1968; Guggenheim & Martin, 1995). Generally, the chemical composition of clay is composed of silica, alumina and water with minor quantity of iron and alkaline earth (Grim, 1968). Clay is a cheap source of silica and alumina that important in high temperature reaction in ceramic industry, such as production of ceramic tiles.

Clay minerals consist of two basic crystal sheets (Holtz & Kovacs, 1981; Kingery et al., 1991) namely, "Tetrahedral or Silica" sheet (Figure 2.4) and "Octahedral or Alumina" sheet (Figure 2.5). Those crystal sheets will stack together with different bonding and metallic ions in crystal lattice. Clay minerals are hydrated aluminium silicates, which contain hydrogen bonded with oxygen in the tetrahedral and octahedral structure to form hydroxyl (OH) groups (Kingery et al., 1991; Vari, 2002). The OH group has common properties with the water molecules. Therefore, minerals containing OH group have strong affinity with water, which will absorb water easily and retain strongly around their crystal and released only by action of heat. However, the strong attraction between clay minerals and water molecules may create dispersion or viscosity issue during wet milling process, which can be solved by adding deflocculant.

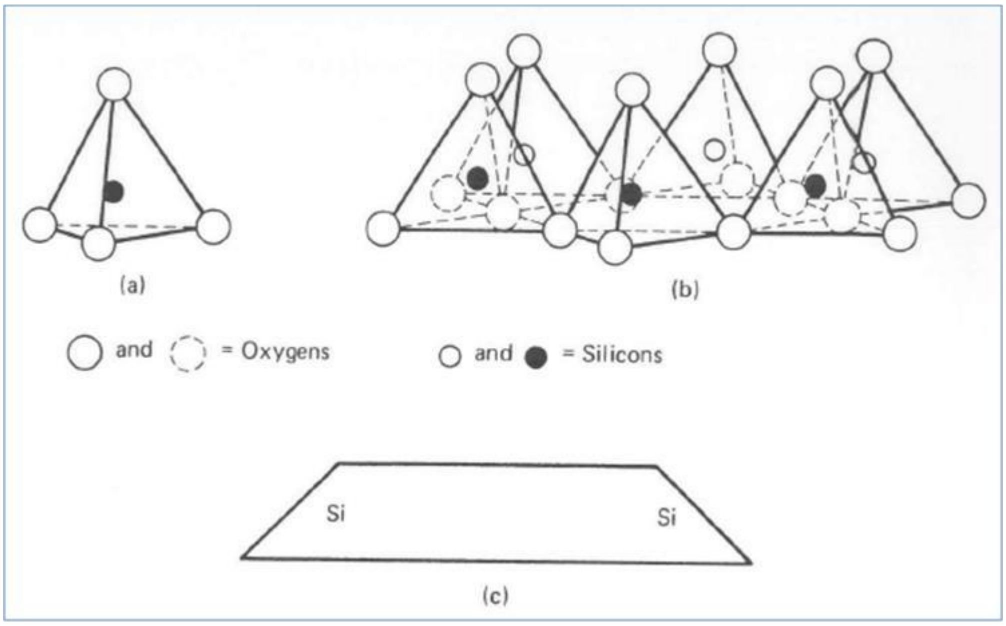

Figure 2.4: (a) Single silica tetrahedron, (b) Isometric view of the tetrahedral or silica sheet and (c) Schematic representation of the silica sheet (Holtz & Kovacs, 1981).

Clay contains clay minerals and other mineral constituents. Clay minerals are the main component of clays and abundant in the surface portion of the earth. The characteristics and properties of clays are mainly derived from the clay minerals which occurred naturally. Clay is usually composed of number of minerals that make up clay. Clay minerals are fine-grained and usually with platy form of structure with particle size of below 2 μm (Arnott, 1965; Gee & Or, 2012). Evaluation of the properties of clay minerals in research work is crucial to determine its application to specific ceramic products.

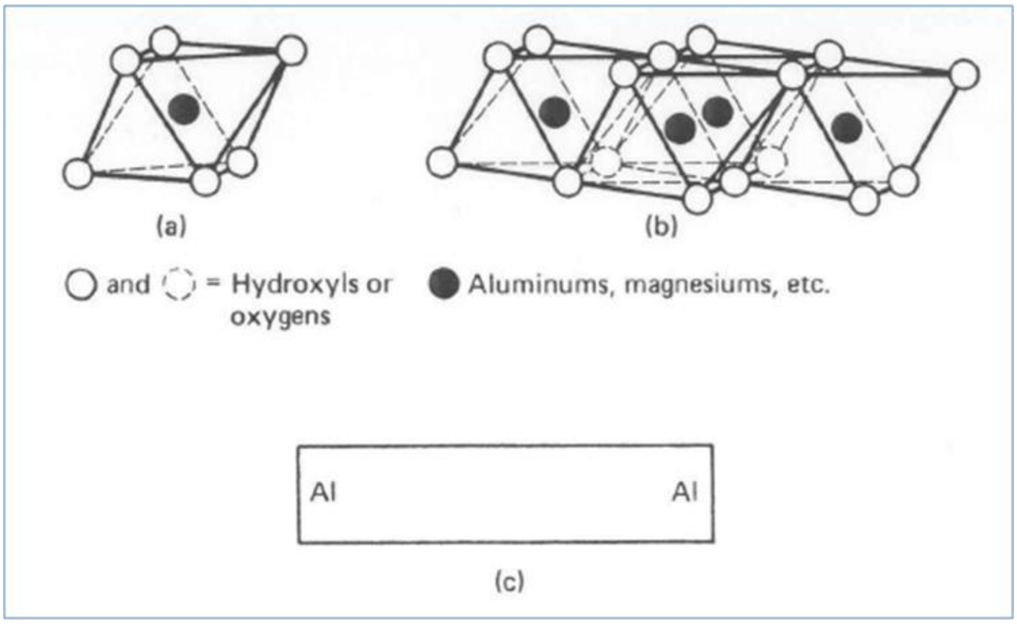

Figure 2.5: (a) Single aluminum (or magnesium) octahedron, (b) Isometric view of octahedral sheet and (c) Schematic representation of the octahedral or alumina sheet (Holtz & Kovacs, 1981).

2.4 Classification and Characteristics Clay Minerals

The suitability of different clay minerals in manufacturing of ceramic tiles is highly dependent to their mineralogical and chemical compositions (Escalera et al., 2014). Clay minerals can be classified to many groups such as kaolinite, montmorillonite and illite, which will be discussed in the following sections.

2.4.1 Kaolinite Group

Kaolinite is widely used in various applications of ceramic industries such as pharmaceutical, paper industry and paint industry (Benea & Gorea, 2004; Ayadi et al., 2013). Kaolinite is one of the most abundant minerals in soils and sediments. It is a common weathering product of tropical and sub-tropical soils (Salahudeen et al., 2015). The term “Kaolinite” origin from Chinese word “Kauling” means “High hill”, which is considered as primary origin from mother rocks that not undergo any shifting or erosion process (Biff, 2003). Kaolinite deposit is usually consists of mixture of kaolinite, quartz, feldspar, mica and iron oxides as minor minerals.

Kaolinite consists of repeated layers of one tetrahedral (silica sheet) is connected to one octahedral (alumina sheet), which is illustrated in Figures 2.6. Basic layers kaolinite structure was held together by hydrogen bonds between hydroxyls of the octahedral (O) sheet and the oxygen of the tetrahedral (T) sheet. Kaolinite is a low layer of 1:1 silicate (TO) structure with thickness of 1:1 (TO) layer of about 0.7 nm (Ayadi et al., 2013; Salahudeen et al., 2015). The very strong hydrogen bonds are preventing the hydration process and allow the layers to stack up to form large crystal.

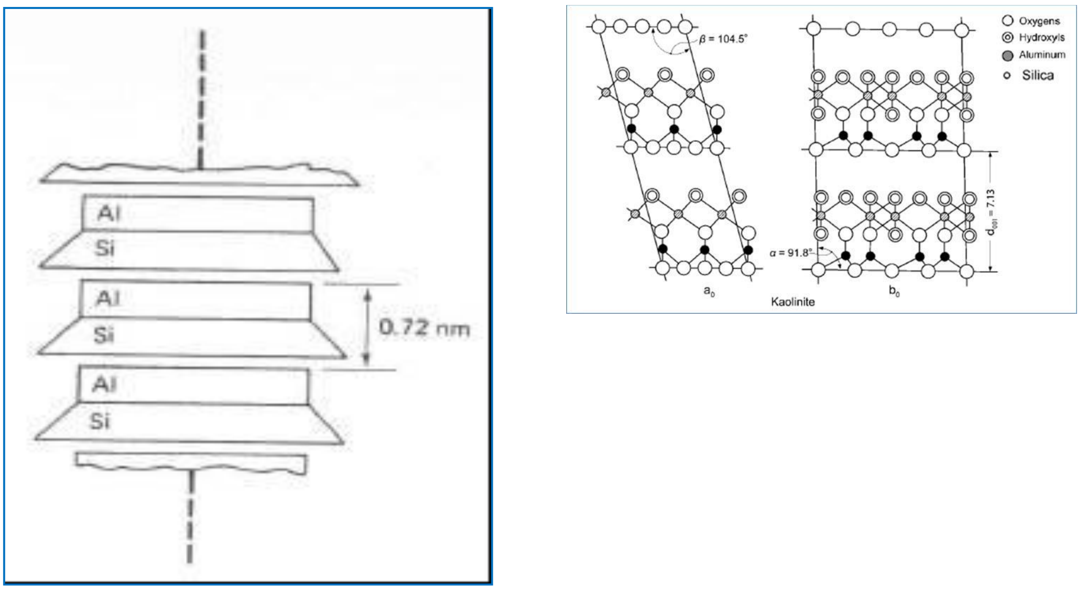

Figure 2.6: Schematic diagram of the kaolinite structure (Holtz & Kovacs, 1981; Murray, 2007)

The mineralogical term for kaolinite is referred to hydrated aluminium silicate [$Al_2Si_2O_5(OH)_4$] or [$Al_2O_3.2SiO_2.2H_2O$] with theoretical chemical composition of SiO_2 = 46.54 %, Al_2O_3 = 39.50 % and H_2O = 13.96 % (Biff, 2003; Murray, 2007). Kaolinite is usually characterized by the present of high aluminium oxide and water with almost absence of alkalis, which makes it a refractory material. The present of high quantity of water in crystal structure leads to large changes in size (i.e., shrinkage) during firing process. The kaolinite rich clay is usually white or nearly white in raw colour, low in iron, white in fired colour and required high vitrification temperature (Grim, 1968; Souri et al., 2015). Clay with highly kaolinite content is very important to ceramic tile industry. The excavation of clay with kaolinite as main minerals in Malaysia is mainly located at Perak, Pahang and Johor. The highest excavation and production of kaolin was recorded in Perak and the lowest by Pahang in year 2016 as shown in Table 2.1 (Iszaynuddin et al., 2016).

Table 2.1: Production of kaolin in Perak, Pahang and Johor from year 2014 – 2016 (Iszaynuddin et al., 2016)

State	**Year (Tonnes)**		
	2014	**2015**	**2016**
Perak	102,579.00	170,724.00	203,719.52
Pahang	87,000.00	45,800.00	71,000.00
Johor	30,072.60	78,169.00	118,212.62
Total	219,651.60	294,693.00	392,932.14

2.4.2 Montmorillonite Group

Montmorillonite is also called as smectite, where the mineral consists of two tetrahedral (silica sheet) and one octahedral (alumina sheet) structure (Figures 2.7) with a weak Van der Waal's bond between single unit structure. The weak Van der Waal's bond between the tops of the tetrahedral sheet causes a net negative charge deficiency in the octahedral sheet and water exchangeable ions can enter and separate the layers (Holtz & Kovacs, 1981).

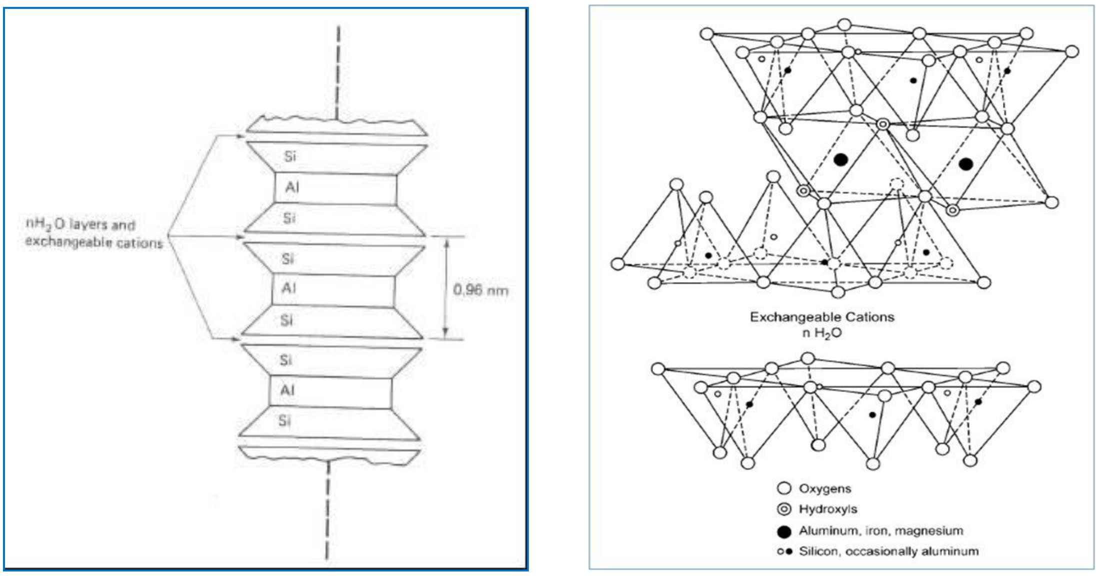

Figure 2.7: Schematic diagram of Montmorillonite structure (Holtz & Kovacs, 1981; Murray, 2007)

Clay containing montmorillonite minerals are susceptible to swelling as water enters the structure, thus increasing the effective volume occupied by the solid and cause an increase in viscosity (Worrall, 1986). The montmorillonite rich minerals in raw formed are giving a soapy feel when rubbed between fingers. Murray (2007) reported that the very fine particle size, swelling capacity and flake shape give montmorillonite the ability to form almost impermeable membranes, which makes it a very good sealant. Furthermore, montomorillonite minerals have good plasticity and bonding properties that give dry compression strength together with good flowability, permeability and durability.

Bentonite is considered as important and complex clay containing high proportion of montmorillonite mineral as main mineral constituent (Reed, 1989). Bentonite is swelling montmorillonite clay with sodium as exchangeable ion, very fine particle, high plasticity, absorb water and can swell up to five times from its dry state due to weak Van der Waal's bond (Sow, 2000; Lynette Chan, 2006).

2.4.3 Illite Group

Illite mineral was first discovered by Professor R. E. Grim of the University of Illinois (Biff, 2003). Illite mineral is described as colloidal mica-like mineral commonly found in clay sediments (Holtz & Kovacs, 1981). The characteristics of illite mineral was referred as aluminium-potassium mica-like, non-expanding and dioctahedral mineral that present in the clay fraction. Illite is usually present together with other minerals such as kaolinite, smectite and chlorite (Ferrari & Gualtieri, 2006). Illite mineral is a fine-grained material but consists of lower potassium content and more water than muscovite (Ryan, 1978; Worrall, 1986).

Figures 2.8 shown the illite structure constituent by the repetition of tetrahedral-octahedral-tetrahedral (T-O-T) layers with the illite structure as montmorillonite-like structure with potassium atoms are bonded in between (T-O-T) layers. The approximate formula for illite mineral can be written as "$K_{0.88}Al_2(Si_{3.12}Al_{0.88})O_{10}(OH)_2X_nH_2O$". Example of chemical composition of pure illite from Kaube (Japan) with "SiO_2 = 47.4 %", "Al_2O_3 = 35.6 %" and "K_2O = 9.12 %" with "Fe_2O_3 = 1.50 %" (Grim, 1939; Ferrari & Gualtieri, 2006). Large percentage of potassium oxide contained in crystal lattice of illite leads to higher fusibility than kaolinite mineral and undergoes lower shrinkage during firing due to its lower water content (Venturelli & Paganelli, 2007).

Illite mineral is an important component of clays that used by ceramic industry as a fluxing material (Wattanasiriwech et al., 2009). The fine particle size and high in potassium content with lower melting point of illite mineral will serve as