CHARACTERISTICS OF KAOLIN FROM EASTERN KINTA VALLEY AND ITS POTENTIAL FOR INDUSTRIAL USES

by

KHONG LING HAN

Thesis submitted in fulfillment of the

requirements for the degree of

Master of Science

November 2018

ACKNOWLEDGEMENT

First and foremost, I would like to express my sincerest appreciation to my supervisor Dr. Hareyani Zabidi for giving me support, guidance, and encouragement thorough the period in completing the degree. The dissertation would not be completed without her supervision and advices. Sincere gratitude is also offered to my co-supervisor Prof. Madya Dr. Kamar Shah Ariffin for his guidance and suggestion thorough the research work.

Secondly, I hope to express my appreciation and gratefulness to AUN-Seed/Net scholarship program for providing financial support to complete my study. Special thanks also to the dean of School of Materials and Mineral Resources Engineering, Prof. Dr. Zuhailawati Bt. Hussain, and the AUN-Seed/Net coordinator in USM Engineering Campus, Prof. Dr. Ahmad Fauzi Bin Mohd Noor who had been sincerely and resolutely in assisting students to solve the other issues they are facing during the period of completing the degree.

Last but not least, gratitude must be conveyed to School of Materials and Mineral Resources Engineering and all its other staffs who had been helpful in supporting me on completion of my degree. Special thanks are given again to Ceramic Research Company Sdn. Bhd. for their technical support and facilities on assisting my research work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVATIONS

AIPEA	Association Internationale pour l'Etude des Argiles
ASTM	American Standard Testing Method
BL	Bukit Lampas
CHN	Carbon, hydrogen and oxygen
CIE	International Commission on Illumination
CMS	Clay Mineral Society
DTA	Differential thermal analysis
E	East
FTIR	Fourier transform infrared spectroscopy
ICDD	International Centre for Diffraction Data
ISO	International Organization for Standardization
LL	Liquid limit
LOI	Losses on ignition
MOR	Modulus or rupture
NW	North west
PDF	Powder diffraction file
PI	Plasticity index
PL	Plastic limit
PSD	Particle size distribution
TRSA	Tanjung Rambutan slope A
TRSB	Tanjung Rambutan slope B
TRSC	Tanjung Rambutan slope C
FESEM	Field emission scanning electron microscope

XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF SYMBOLS

Å	Armstrong
cm	Centimeter
ºC	Degree celcius
g	Gram
m	Meter
mg	Milligram
Mpa	Million pascal
µm	Micron

CIRI-CIRI LEMPUNG KAOLIN DARI TIMUR LEMBAH KINTA DAN POTENSINYA UNTUK APLIKASI PERINDUSTRIAN

ABSTRAK

Kaolin adalah sumber mineral yang memaparkan ciri-ciri yang sangat berbeza apabila ditemui di alam semulajadi disebabkan oleh perbezaan dalam konteks geologi di lokasi yang terbentuk. Setiap mendapan kaolin memerlukan kajian yang mendalam untuk mencapai pemahaman yang lebih baik mengenai proses kaolinisasi. Dalam tesis ini, geologi kaolin yang baru ditemui timur Lembah Kinta, Malaysia telah diterokai melalui penyiasatan singkapan dan analisis geokimia.Kaolin ini telah dicirikan dari segi komposisi kimia dan mineralnya, bersama cirian tekstural, fizikal, kimia, termal dan seramik untuk menilai potensi dalam aplikasi perindustrian. Teknik pencirian termasuk PSD, FESEM, S.G., had atterberg, pengukuran warna, XRD, FTIR, XRF, DTA / TG dan sifat jasad bakar (kadar pengecutan, kadar penerapan air, modulus pecah), dan keputusan tersebut telah dibandingkan dengan sampelmendapan yang telah dikenali (Bukit Lampas). Kajian geologi mencadangkan bahawa kaolin berasal dari mikrogranit leukokratik yang telah diubah secara hidrothemal, dan granit ini yang telah dikaolinisasi t terdiri daripada hampir keseluruhannya adalah kuarza dan mineral kaolin dengan kandungan alkali dan fasa pembawa tinaniaferrous yang sangat rendah. Pencirian mendapati kaolin lembut tipikal yang mungkin juga halosit telah mengantikan kaolinit halus berkeping di dalam pecahan kaolin. Kaolin mempunyai ciri mencetak yang sederhana serta sifat optik dan refraktori yang sangat baik, oleh itu sesuai untuk digunakan dalam pengeluaran seramik atau porselin berwarna putih yang mementingkan kecerahan dan keputihan. Kajian ini mempersembahkan sejenis mod

mendapan kaolin baru di Malaysia yang berpotensi untuk dibangunkan menjadi sebuah kawasan perlombongan kaolin baru.

CHARACTERISTICS OF KAOLIN FROM EASTERN KINTA VALLEY AND ITS POTENTIAL FOR INDUSTRIAL USES

ABSTRACT

Kaolin is a mineral resource which exhibits highly variable properties when found in nature due to the differences in geological context at the location they formed. All kaolin deposit requires a deep study to achieve a better understanding of the kaolinization process. In this thesis, geology of a newly discovered kaolin from eastern Kinta Valley, Malaysia were explored through outcrop investigation and geochemical analyses. The kaolin was also characterized in term of its chemical and mineral composition, plus the textural, physical, chemical, thermal and ceramic properties to evaluate its potential for industrial application. Characterized techniques included PSD, FESEM, S.G., atterberg limits, colour measurement, XRD, FTIR, XRF, DTA/TG and fired properties (firing shrinkage, water adsorption, modulus of rupture), and the results were compared to reference sample from an established deposit (Bukit Lampas). Geological study suggests that the kaolin is derived from hydrothermal alteration of leucocratic micrograniite, and the kaolinized granite consists almost entirely of quartz and kaolin minerals with extremely low content of alkali and tinaniaferrous bearing phases. Characterization of the washed clay had found that it is the typical soft kaolin which may have halloysite substituted for the fine platy kaolin in the clay fraction. The kaolin has moderate moulding properties but superior optical and refractory properties, thus ideal for production of whiteware or porcelain which demands extreme brightness and whiteness. This study presents a new mode of kaolin occurrence in Malaysia with potential to be developed into a new kaolin mining region.

CHAPTER ONE

INTRODUCTION

1.0 Introduction to kaolin

Kaolin is a versatile industrial mineral widely used by various industry when appearance of the finished product is important (Ariffin et al., 2008). Kaolin possess several characteristics such as high brightness and whiteness, soft and non-abrasive, chemically inert, low inner charge, low base exchange capacity, low electrical and thermal conductivity, ability to withstand high temperature, low viscosity, low absorption capacity, platy hexagonal crystal shape, and low surface area when compare to other clay minerals, making it an ideal material for various applications (Murray, 2000). Kaolin was first mined for making of high quality china or ceramicware (Chen et al., 1997). Largest consumers of kaolin at present included the paper, paint, rubber, plastic, ceramic, refractory and glass fibre industry (Siddiqui et al., 2005; Sengupta et al., 2008;). Other than that, small amount of kaolin is used in production of portland cement, pesticides, and pharmaceutical products (Kogel et al., 2006). During the year of 2017, 37,000,000 tons of kaolin were being produced worldwide to supply the demand globally (USGS, 2018). Deposit of kaolin, especially the high-quality one is a highly valuable natural resource which can aid in country development if the resource is managed properly.

1.1 Occurrences of kaolin

Kaolin is a ubiquitous clay material extensively distributed over earth's surface. It is the most abundant clay mineral in the overlying soils on earth surface, and kaolinite is by far the most common kaolin mineral to present on earth (Aras et al., 2007). However, despite the abundant presence of kaolin in soil or rock over all continents, large high-purity kaolin deposits capable of supplying large processing facilities and are accessible to global transportation infrastructures are rare (Kogel et al., 2006). At present, there are kaolin deposits discovered with extremely large reserve and exceptionally good quality of clay that are mined to market worldwide. Deposits able to full fill these two criteria are classified as major world class deposits. Table 1.1 listed some of the world class kaolin deposits being mined at present. The kaolin produced from these deposits are generally utilized for higher end application due to the superior quality of these products, and the consistency on quantity and quality of clay they can provide. A statement on one of the largest kaolin producing country, China should be made here. China does not consist of any large company or deposits comparable to those discussed in Table 1.1, but the total volume of kaolin produced by small kaolin industries scattered thorough the country had achieved an annual production of 2,000,000 tons of kaolin (Wilson, 2004).

On the other hand, smaller deposits scattered around the world are being developed to support local demand of poorer quality clays. Small scale kaolin mines are usually operated by smaller mining companies, with the supply chain targeted to the neighbouring industries. Only simple and small capacity processing facilities are being incorporated for beneficiation process to produce lower grade products for supplying of neighbouring industries as rubber fillers (Aw, 1983), or as raw material for traditional ceramics products (Adeola, 2015; Chin et al., 2017). Transportation cost is an important factor for these industries on selecting their supply (Bun, 2012). These deposits are less likely to receive attention from large mining companies due to poor accessibility and smaller reserve volume.

Table 1.1: Location, reserve and application of some major world class kaolin deposits (Murray, 2007).

Secondary Kaolin	
Georgia and South California area of USA	500,000,000 tons of proven reserve.
Amazon river, Northern Brazil	> 500,000,000 tons proven reserve, primarily used to produce ultra-fine glossing pigment for paper coating (Kogel, et al., 2006).
Primary Kaolin	
Cornwall and Devon area of UK	Produced over 170,000,000 tons of processed clay, application included paper filling and coating, paint, adhesives and sealants, rubber, tiles, plastics, and ceramics industries (Manning, 1995).
Karlovy Vary of Czech Republic	100,000,000 tons proven reserve, mainly used as ceramic raw material.
Bangka and Belitung Island at north of Jakarta, Indonesia	Produced clay applied as ceramic raw material, paper filler.
North Island of New Zealand	Halloysite mine, raw material for fine china ceramic.

In term of defining the resources, smaller mining companies may not be capable to perform a proper exploration and study on the deposit. Cooperation between mining companies with scholars or academicians to investigate and survey these occurrences may be helpful to ensure that exploration program is systematically and appropriately conducted. Some examples of studies on smaller scale kaolin occurrences by worldwide scholars are listed in Table 1.2. Studies had been conducted on various aspects regarding clay occurrences, which included the geology, geochemistry, origin, mineralization pattern, quality, several engineering properties and potential of the clay for industrial uses. Through their publications, information on these clay occurrences are readily accessible by interested parties, which can assist in planning of exploration in future and to determine suitable function(s) for the clays.

Table 1.2: List of literature on study performed by worldwide scholars on their local kaolinitic clay occurrences.

Location	Year	Scholar
Assin-Fosu and Kumasi, Ghana	2017	(Yaya, et al., 2017)
Nagar Pakar, Pakistan	2015	(Ismail, et al., 2015)
Jiangxi, China	2014	(Yuan, et al., 2014)
Ekiti, Nigeria	2014	(Akinyemia, et al., 2014)
Sinai, Egypt	2013	(Masoud, et al., 2013)
Africa	2010	(Ekosse, 2010)
Afyon and Istanbul, Turkey	2010	(Celik, 2010)
Algaof, Yemen	2009	(AL-Shameri & Rong, 2009)
Mayouom, Cameroon	2006	(Nyoja, et al., 2006)
Swat, Pakistan	2005	(Siddiqui, et al., 2005)
Kerri-Kerri, Nigeria	2004	(Shemang, et al., 2004)
Kgwakgwe, Botswana	2001	(Ekkose, 2001)
Neuquen, Argentina	1997	(Cravero, et al., 1997)

1.2 Study area

The study area is located at the eastern part of Ipoh or Kinta Valley. The primary kaolin extends from Tanjung Rambutan to Simpang Pulai of Hulu Kinta District, Perak. The area is located 10 km east of the capital town of Perak, Ipoh. Tanjung Rambutan was historically famous of tin mining during 1880s (Khoo & Lubis, 2005). Few of the largest and most well know tin mines at the age included the Kinta Association (1903), Rambutan Ltd (1905), and Rambun Mines Hydraulic Tin Ltd. (1925). An overview map showing the study area is shown in Figure 1.1.

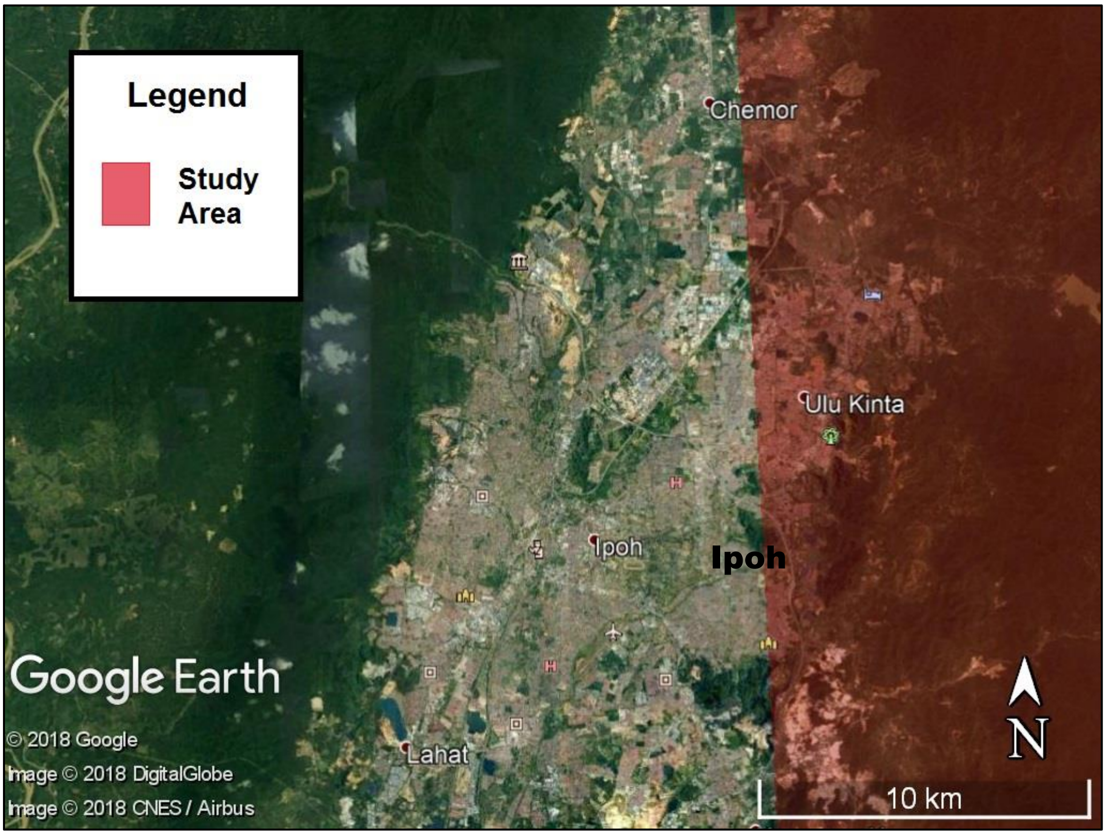

Figure 1.1: Overview map showing location of study area.

1.3 Problem statement

Deposition of pneumatolytic kaolin had been reported to associate with tin deposits in Kinta Valley and exploitation had begun since 1920s (Ingham & Bradford, 1960). The operation however was operated in small scale and lasted only for few years, until further mining was limited by the water level. No follow-up survey or further exploration had been conducted for the primary clay deposit, as mining activities was focused mainly on tin. At present, Malaysian kaolin is mainly exploited from the granitoid and schist hosted deposit located in between Bidor and Tapah, Perak (Cheang, et al., 2013). Half or more of the kaolin produced in Malaysia were originated from the Bidor Tapah area (JMG, 2015). Kaolin from Kinta Valley had not been receiving attention until a leucocratic microgranite or aplite hosted kaolin deposit recently being discovered at Simpang Pulai. The kaolin deposit had been studied and evaluated by Ariffin et al. (2008), Baioumy (2012) and Chin et al. (2017) but not in sufficient depth due to the low and insignificant volume of the deposit. As more outcrops of kaolinitic clay occurrence which exhibit similar geological characteristics continue to be unveiled, more information regards the kaolin are viable to be collect at present. This study is conducted to investigate the geology of the occurrences and provide an overview on the characteristics of kaolin from Eastern Kinta Valley by considering samples from more location. Study of new kaolin deposits in different parts of the world could be very important, since every place has different geological context and new data could contribute to better understand the kaolinization process. Although there are many examples in the world, new deposit will require a very deep study. The study hopes to identify and highlight a potential mineralization zone of the kaolin for further exploration, with the quality or suitable application of the clay being reported concurrently.

1.4 Objective

The objective of this thesis is to:

I. To investigate the geology of kaolin from Eastern Kinta Valley.

II. To characterize the technical properties of kaolin from Eastern Kinta Valley.

III. To determine the potential industrial application(s) for the kaolin.

1.5 Research approach

Field survey is a crucial part for investigation of a geological occurrence. Outcrop were identified and located through geological mapping. Field survey was then conduct on identified outcrops and samples of rock or clay were collected from field for laboratory analysis. Geology of the kaolin will then be discussed based on description of outcrop and hand specimens supported by geochemical studies.

Representative clay samples are collected for laboratory analysis to determine the industrial properties. The analysis involves characterization of the clay in term of its chemical and mineral composition, together with textural, physical, chemical and thermal properties. These properties were then used to evaluate and determine the potential of the clay for industrial applications.

1.6 Thesis outline

The content of each chapter is outlined as follows:

Chapter one: This chapter provides a brief overview on the natural occurrences of kaolin and their uses, current trend of kaolin supply and demand, either worldwide or locally. The problem statement, objectives and research approaches to achieve the prescribed objectives were also described in this chapter.

Chapter two: This chapter firstly discusses the fundamental theories and knowledge that are necessary for study of clay science. The crystal morphology, formation and natural occurrences of kaolin are being discussed. Processing technology of kaolin and important properties of kaolin regarding its applications is then reviewed.

Chapter three:. This chapter consists of two major part in which the first part deals with the geological investigation. A brief history on the kaolin industry and occurrence in Malaysia is being described, then the general geology of study area is reviewed with more specific location and background of outcrops of kaolin occurrence being described. The techniques used in the geochemical study of kaolin formation are then discussed. The second part discusses the techniques used in characterizing and washing the raw clay, follow by methods to assess of the washed clay in term of its textural, physical, chemical, thermal and firing properties.

Chapter four: This chapter is consisting of two major parts, which the contents are directly correlated to the objective of this thesis. The first part discusses findings regards the geology of kaolin formation through its field occurrences, physical and geochemical characteristics. The second parts describe the result of characterization and evaluation of the clay in term of its chemical and mineral composition, together with textural, physical, chemical and thermal properties. The fired behavior of washed clay is also discussed. Finally, a summary regards the finding and its interpretations on potential application(s) of the clay are provided.

Chapter five: Conclusions regards the finding in chapter five which answer the three objectives of this thesis is given in this chapter. Recommendations of further follow up action are also given.

CHAPTER TWO

LITERATURE REVIEW

2.0 Definition of “Clays” and “Clay Minerals”

The definition of “clays” and “clay minerals”, and the objects of study of this science continue to evolve with the development of technology, which enable more precise characterization of fine grained materials that was previously impossible (Guggemheim et al., 2006). The increasing capability of present analytical instrumentation and methodologies such as X-ray diffraction, spectroscopy (Infrared, Raman), scanning electron microscopy associated with X-ray energy dispersive spectrometry, and synchrotron X-ray diffraction have played essential roles in modern clay research (Bergaya et al., 2006).

However, with all the available characterization techniques, there is no single definition which able to satisfy all members of community at present. Complication arises due to the inappropriate definition of “clays” is question by various researchers, such the requirement on particle size limit of clay (Weaver, 1989), requirement on clay to be naturally occurring or as a result of geological processes by (Nickel, 1995), or the necessity on ability of clay to impart plasticity with a certain moisture content as stated (Grim, 1968). Rautureau et al. (2017) however considered that the flaws are tolerable as clay is most probably the mineral resource exhibiting the highest variability in geologic, textural, and mineralogical terms and the most diverse applications, after reviewed the unique definition of clay from every single profession or discipline interested in clay with clay which included geology, sedimentology, petrography, mineralogy, ceramists, pedologists, civil and geotechnical engineering.

There are societies and associations who had been putting effort to provide unifying terminology for “clays” and “clay minerals”. Two of the most important contributors are Nomenclature Committee of the Association Internationale pour l’Etude des Argiles (AIPEA, International Association for the Study of Clays) established since 1966 and Clay Minerals Society (CMS) Nomenclature Committee which established since 1963 (Guggemheim et al., 2006). AIPEA and CMS had been cooperating and actively involved in revising the definition, classification, and terminology of clays, clay minerals, related materials, and specific properties until present (Mackenzie, 1959; Brindley et al., 1968; Bailey et al., 1971; Brindley & Pedro, 1972; Bailey, 1980; Bailey, 1982; Bailey, 1989; Guggenheim & Martin, 1995; Guggemheim et al., 2006; Rautureau et al., 2017). Significant changes have been proposed, developed, and adopted by several authors and clay groups or clay societies over time (Guggemheim et al., 2006). Over time, AIPEA and CMS had both come to concur on some basic criteria that should be included into definitions of “clay” and “clay mineral”. They agreed that clay can be expressed as “naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired.” (Guggenheim & Martin, 1995). The definition does not exert a precise numerical value for the particle size as different disciplines and professions have their own unique limit when defining particle size (Bergaya et al., 2006). Exceptions on material to be considered as clay also being pointed out, such as the flint clay which contains over 95 % of kaolinite but is non-plastic, and materials other than phyllosilicates which can impart plasticity and can harden upon drying and firing.

The term "clay mineral" refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing (Guggenheim &

Martin, 1995). With this definition, the particle may be of any crystallite size so that the term ‘clay mineral’ can correlate with the definition of ‘mineral’, which is unrelated to crystallite size (Guggemheim et al., 2006). Coarser minerals like macroscopic mica, vermiculite, and chlorite may now be regarded as clay minerals (Bergaya et al., 2006).

By comparing the definition of “clay” and “clay mineral”, it is noted that there are some distinctions between them. As discussed above, unlike “clay”, “clay mineral” are not necessary to be fine grained, but rather they may be of any crystallite size. Clay can consist associated minerals other than clay minerals, such as quartz and feldspar, carbonates, oxides and hydroxides of iron and aluminum such as hematite, goethite, gibbsite, and organic matter (Rautureau et al., 2017).

2.1 Crystal structure and classification of clay minerals

Clay minerals are hydrous layer silicates which belong to the family of phyllosilicates (Guggemheim et al., 2006). Crystalline structures of clay minerals are built of stacking of tetrahedral and octahedral sheets. The two-dimensional tetrahedral sheet has composition of T_2O_5 (T = tedrahedral cation, normally Si, Al, Fe...), in which individual shares three of its corners with surrounding tetrahedral to form a hexagonal mesh pattern (Brindley & Pedro, 1972). The fourth corner of tetrahedral at a direction perpendicular to the two-dimensional structure, form parts of an octahedral sheets where octahedral are linked laterally by sharing octahedral sheets. The octahedral sheet comprised of closely packed oxygens and hydroxyls in which Al, Fe, and Mg atoms are arranged in octahedral coordination (Murray, 2007). The smallest structural unit contains three octahedra, and the sheet is classified as dioctahedral sheet if two of the octahedral is occupied by a cation in the centre, or trioctahedral sheet if all three octahedral is occupied (Lazaro, 2015). Occupancy of octahedral is dependent on the charge of center cation to achieve a balance of charge. The term “brucite-like” and “gibbsite-like” may be used to describe the trioctahedral and dioctahedral structure respectively (Guggemheim et al., 2006).

An assemblage formed by linking one tetrahedral sheet to one octahedral sheet is known as 1:1 layer, and it represents the unit structure of the kaolin group minerals (AL-Shameri & Rong, 2009). A 2:1 layer is consisting of two tetrahedral sheets sandwiching an octahedral sheet in between, and it represents structure of pyrophyllite and talc. Micas and chlorites have crystal structures similar to pyrophyllite, but with the tetrahedral Si^{4+} sites substituted by Al^{3+}. The produced net negative charge is balanced by alkali or alkali earth cations attached to the structure, either between layers of repeating structural unit or inside of tetrahedron (Fahrenholtz, 2008). Illustrations of cross section of structure of kaolinite, pyrophyllite and muscovite is shown in Figure 2.1.

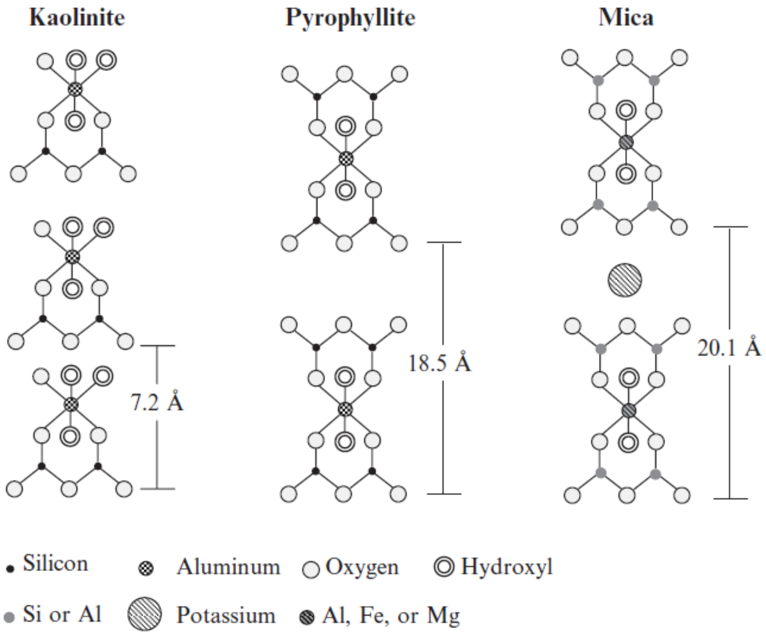

Figure 2.1: Schematic representation of cross section on structure of kaolinite, pyrophyllite and muscovite (Fahrenholtz, 2008).

Clay minerals are distinguished from each other based on the stacking order of octahedral and tetrahedral sheets, plus the various type of interlayer materials such as individual cations, hydrated cations, hydroxide octahedral groups and sheets (Bailey, 1980). The present clay minerals classification scheme are compromises of eight major clay groups, with their layer type, interlayer material, and interlayer charge listed in Table 2.1.

Table: 2.1 Classification of planar hydrous phyllosilicates with their group name, layer type, interlayer material and layer charge respectively (Guggemheim et al., 2006; Brown & Brindley, 1980).

Clay group	Layer type	Interlayer material	Interlayer charge per formula unit, *x*	Basal spacing (Ǻ)
Serpentine - kaolinite	1:1	None or H_2O	~0	7.1
Talc - pyrophyllite	2:1	None	~0	9.3
Smectite		Hydrated exchangeable cation	~0.2 - 0.6	14.0
Vermiculite		Hydrated exchangeable cation	~0.6 - 0.9	14.3
True mica		Non-hydrated monovalent cations (>50%)	~0.85 - 1.0	10.1
Interlayer deficit mica		Non-hydrated mono or divalent cations	~0.6 - 0.85	10.1
Brittle mica		Non-hydrated divalent cations (>50%)	~1.8 - 2.0	10.1
Chlorite		Hydroxide sheet	variable	14.2

2.2 Kaolin

2.2.1 Cyrstal morphology and chemistry

Kaolin group minerals have the simplest unit structures among the eight major clay groups. As illustrated in Figure 2.1, a unit layer of kaolin group minerals is formed by linking one tetrahedral sheet to one dioctahedral sheet (Varga, 2007). This resulted kaolin minerals to have a structural formula of $Al_2Si_2O_5(OH)$ (Newman & Brown, 1987). Kaolinite, nacrite and dickite are grouped together due to on their similar chemical composition and crystal structure and differs from each other by the ordering pattern of vacant octahedral site in subsequent layers (Bailey, 1980). Halloysite on the other hand is formed by rolling of a planar 1:1 layer (Singh & Mackinnon, 1996; Yuan et al., 2015). The layer curls with the tetrahedral sheet on the outside of the curve to minimize the misfit of the larger tetrahedral and smaller octahedral sheets (Bailey, 1990; Singh, 1996). Kaolin minerals generally have specific gravity of around 2.6, which may vary when found in nature (Murray, 2007). Higher specific gravity is generally displayed by hydrothermal kaolin compare to sedimentary kaolin (Baumann & Keller, 1975).

2.2.2 Formation and mode of occurrences

Kaolin is formed by chemical alteration of aluminosilicate or feldspar minerals. The process involves hydrolysis and acid leaching to remove the dissolved alkali cations from feldspar (Ariffin et al., 2008). A simplified version of the decomposition reaction of alkali feldspar into kaolinite is given as in equation 2.1 (Garrels & Howard, 1959):

$$2KAlSi_3O_8 + 2H^+ + H_2O = Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2K^+ \qquad \text{Equation 2.1}$$

The reaction is dependent on the kinetics of surface reactions at the mineral-water interface (Blum, 1994). Complete decomposition of feldspar will result in formation of kaolinite and quartz, and the release of alkali cations. Similar reactions could also be written for sodium feldspar or plagioclase minerals (Earle, 2018). Mica may be encountered as an intermediate product of the weathering process (Fahrenholtz, 2008).

Kaolin or china clay was first discovered at “Gaoling”, a place of China where this earthy material had its name derived (Keller et al., 1980). Kaolin then began to be discovered and mined from other countries and continents. Some major and minor occurrences of kaolin deposit around the world had been discussed in chapter 1. On the other hand, dickite and nacrite may be encountered only in minor amount associated with kaolinite of hydrothermal origin (Murray, 2007). There is no large-scale exploitation of either nacrite or dickite (Jepson, 1984). For halloysite, the largest mine known is at North Island of New Zealand, and Dragon Mine, Utah (Churchman et al., 2016). Kaolin occurrences are classified as primary/residual or secondary kaolin based on their origin (Pruett, 2016). Examples of major well recognized and some smaller scale primary and secondary kaolin deposits are given in Table 1.1 and Table 1.2 respectively.

A. Primary kaolin

Primary kaolins are those that derived in-situ, where the residual texture and structure of the parent rock is preserved (Murray, 2007). The feldspar in parent rocks may be decomposed into clay by surface weathering, or/and hydrothermal alteration (Ismail et al., 2015; Galán et al., 2016). Parent rocks known to host kaolin deposit included granites (Kitagawa & Koster, 1991; Masoud et al., 2013), phyllite (Wilson & Jiranek, 1995), arkose (Varajao et al., 2001), metaarkose (Schwaighofer & Mueller, 1987), rhyolite and tuff materials (Sayin, 2007; Yuan et al., 2014). Extend of kaolinization in hydrothermal kaolin deposit depends largely on the discontinuity features in hosting rock (Swindale & Hughes, 1968; Erkoyun & Kadir, 2011). The faults, joints, and fractures served as passage for circulation of acid hydrothermal fluids to decompose the feldspar minerals. For surface weathering, kaolin is form by in-situ weathering of underlying rock exposed to atmosphere (Varajao et al., 2001). The degree of kaolinization usually decreases with depth, as is often found in a weathering profile (Wilson & Jiranek, 1995). Other properties such as porosity and permeability of the rock, and the presence of joints and fractures can also affect decomposition of the rock. Kaolinization by surface residual weathering had reported to extend to a depth of 50 m in a highly jointed and faulted granite in Czech Republic (Wilson & Jiranek, 1995). Common impurity minerals encountered in primary kaolin are those with resistance to alteration which included quartz, muscovite, tourmaline and zircon, while incomplete altered parent rock may consist minerals originally present in parent rock such as phenocrysts of feldspar and biotite, or minerals that are the first series product of chemical alteration such as halloysite, illite, vermiculite, and/or smectice (Kogel et al., 2006).

B. Secondary kaolin

Secondary kaolins are kaolin formed by sedimentary depositional processes (Ismail, et al., 2015). Deposition of kaolin clay can occur at sedimentary basin or lower energy environment (Abedini & Calagari, 2015). During the process of transportation, most of the grits are sorted out from the clay by wind, water and gravitational activity, leaving the secondary deposit to has a significant higher clay minerals content. Grits are defined as particle larger than 44 μm, and usually consist of quartz, mica and a suite of heavy minerals (Murray, 2007). This is best explained when refer to the typical example of primary and secondary kaolin deposit. The primary kaolin deposit in

Cornwall, England has recoverable clay content of only 15 %, when compare to the secondary kaolin from Georgia-Carolina with a recoverable clay content of over 90 % (Jepson, 1984). On the other hand, clay sized impurities included anatase, illite, smectite, hydroxyl-interlayer vermiculite, mixed-layered clay minerals, goethite, hematite and organic matter are more commonly present in secondary kaolin (Kogel et al., 2006).

2.2.3 Chemical and mineral composition

The ideal chemical composition of a pure kaolin clay, consists only perfectly crystallized kaolin minerals is SiO_2, 46.54 %; Al_2O_3, 39.50 %; and H_2O, 13.96 % (Newman & Brown, 1987). Composition of kaolin from nature however always differ from ideal. In nature, kaolin is found as a rock comprised essentially of kaolinite and/or the other kaolin minerals such as dickite, nacrite, and halloysite (Murray, 2007). Other mineral impurities such as quartz, anatase, rutile, pyrite, limonite, feldspar, mica, montmorillonite, and various titanium oxides, iron oxides and hydroxides are commonly associated with the clay (Weaver & Pollard, 1973). As a result, Fe, Ti, Mg, Ca, K and Na are nearly always detected in kaolinite samples. Presence of quartz and gibbsite causes samples to have excess of SiO_2 or $A1_2O_3$. Isomorphous substitution of centre cations in tetrahedron and octahedron can also lead to variation in chemical composition of kaolin minerals (Barton, 2002).

Some the impurities in kaolin clay can significantly deteriorates the clay quality, even if only presence in minor amount. Examples of major impurities which greatly reduce the value of kaolin deposits include:

(1) titanium oxides, iron oxides and hydroxides which discolours the clay to off white (Bertolino, et al., 2010; Cheang et al., 2013),

(2) smectites and halloysite which adversely influence the rheological behaviour of kaolin slurries

(3) abrasive fine-grained silica and fine-grained feldspar which causes undue wear to process machinery especially in paper production (Manning, 1995).

When used as ceramic raw material, presence of alkali and alkali earth elements can affect the thermal behavior of clay. They reduce the refractory properties of the clay but may be favorable by ceramic producers who fire their products at lower temperature to achieve a better vitrification (Chin et al., 2017).

2.4 Processing of kaolin

Processing and beneficiation of kaolin clay aims to extract or purify the clay fraction from kaolin ore. The processing methods of kaolin is selected based on the quantity and nature of impurity minerals associated with it and the end use of the material (Ramaswamy, 2007). The properties of impurities in kaolin from different deposit however can vary a lot and induces different degree of complexity to the removal of impurities. For example, free silica, one the most common impurity in kaolin can have different effects on the beneficiation process. Free silica, when present in granite, are usually coarser in size due to the longer period of crystallization process and can be sorted out easily from the clay by conventional gravitational separation method or degritting process. Free silica in volcanic rocks however can induce a level of difficulty to the separation process. They can presence as micro crystalline or alunite, which are much finer in size (Manning, 1995; Sayin, 2007). The difficulty of separating them from clay increase when they have size closer to the clay particles. The problem can even become more complicated when the free silica is porous. The particle tends to have lower strength and may be breakdown into finer size particles during the beneficiation process, leaving them inseparable from the kaolin. Similar applied to the clay sized impurities present in secondary kaolin deposit.

After all, most impurities in mineable kaolin deposit are separable through size fractionization processes, which can be classified into dry and wet method (Murray, 2000). More extensive description on the method and the involved processes are given in section below. Depending of the purity of clay, processes such as magnetic separation (Bertolino et al., 2010; Santos et al., 2012), flocculation (Murray, 2000), flotation (Liu et al., 2017) and acid bleaching (Silva et al., 2009; Silva et al., 2011; Taran & Aghaie, 2015) may be used to further refine the clay product by removing the iron and titanium bearing phases of clay sized fraction. After all,

2.4.1 Wet method

A detailed elucidation of the wet processing of kaolin had been given by (Murray, 2007) and included as Figure 2.2. The first stage involves the preparation of kaolin into a stable dispersion where agglomerations are broken down into individual particles must be produced (Bailey, 1980). A dispersed pulp of kaolin is produced by blunging the ore with water and a small percentage of a chemical dispersant. The solid content in pulp can be up to 60%. Uses of dispersant is necessary to hinder the agglomeration of discrete particles. Dispersants introduce cations into the pulp which attach to the negatively charged surface of clay particles, thus prevent formation of hydrogen bond between the positively charged edges and negatively charges basal surface of kaolinite particles (Konduri & Fatehi, 2017). The commonly used chemical dispersants which included sodium silicate, sodium hexametaphosphate (Calgon), or tetrasodium pyrophosphate (TSPP), is added in an amount ranging from 0.2–0.6% of the kaolin dry weight (Stempkowska et al., 2017; Penkavova et al., 2015). Once the kaolin is dispersed, the pulp is subjected to degrittation follow by classification processes (Ramaswamy, 2007). Degrittation firstly involve removal of coarser grits by passing the pulp through sluice box or spiral classifier, follow by separation of finer grit using hydrocyclone (Manning, 1995). The degritted pulp is then pumped to a processing plant where kaolin particles are sorted into different size fraction through a series of centrifuges or hydrocyclones, or hydroseparator (Murray, 2007). A kaolin product with desired particle size distribution is produced after this stage and can be marketed after processed into dried powder form, filtration cake or even directly as slurry. On the other hand, coarser kaolin fraction from produced this stage can be marketed directly as coarse filler products, or as feed for production of delaminated kaolin (Bloodworth et al., 1993).

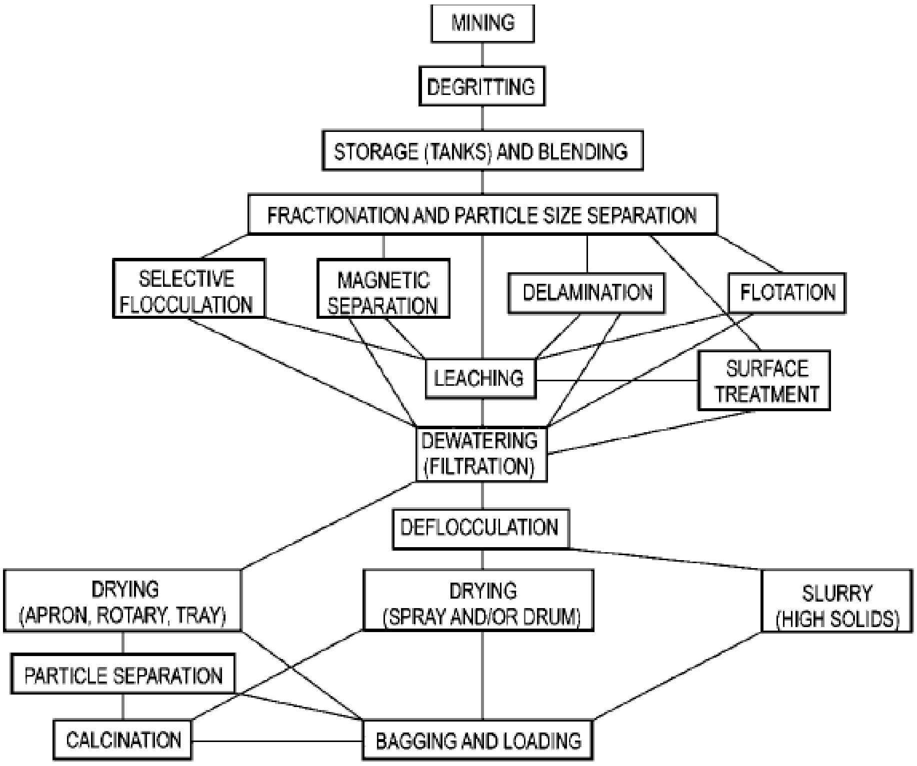

Figure 2.2: Processing circuit of kaolin by wet method (Murray, 2007).

2.4.2 Dry method

The dry processing of kaolin is relatively simple and is associated with lower processing cost and poorer degree of refining when compare to wet method (Kogel, 2014). The general flowsheet utilized in dry process is shown in Figure 2.3.

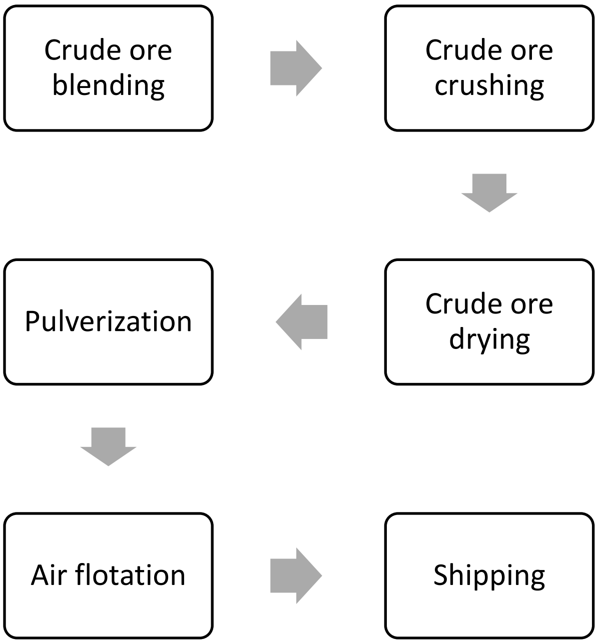

Figure 2.3: Processing circuit of kaolin by dry method (Murray, 2007).

The processes are simply crushing, drying, pulverizing and classification of particle by air flow. The essential feature of the dry process is to dry the raw clay until it can be pulverized without agglomerate. Pulverized products are separated into fraction of different size in air classifier, where the coarse fraction leaves as underflow, and fine fraction leaves as overflow. Underflow product may be impounded directly or recycled as feed to pulverizing mill to recover previously unliberated clay. Fine particle size products are produced from dry method. The highest quality of kaolin produced by dry method is for filler application, with the uses of highest quality raw kaolin as feed into the circuit (Prasad et al., 1991).

2.5 Textural properties (Shape, size and crystallinity)

Textural properties are among one the fundamental properties especially important to be understood as they have direct influence on the other properties related to the applications of kaolin such as plasticity, brightness, firing behavior and rheological properties of kaolin. The texture of a clay material refers to the particle size distribution of the constituents, the particle shape which is related to the morphology and the orientation of the particles with respect to each other (Murray, 2007). Kaolin clays are classified into soft and hard kaolin based on their shape and size. Soft kaolin is coarser in size and consists mainly of stacks of euhedral crystallites, while hard kaolin is typically made up of finely sized single crystal platelets (Kogel et al., 2006; Pruett, 2016). Hard kaolin has lower crystallinity than soft kaolin (Hinckley, 1965). In order to quantify the degree of crystallinity, Hinckley proposed the use of kaolinite crystallinity index which computing the degree of crystallinity of kaolin samples from X-ray powder diffraction patterns (Plancon, et al., 1988). This index is the ratio of "the sum of the heights of the reflections $(1\bar{1}0)$ and $(11\bar{1})$ measured from the inter-peak background" to "the height of the $(1\bar{1}0)$ peak measured from the general background". The method to determine height of $(1\bar{1}0)$ and $(11\bar{1})$ peak from inter-peak background, and height of the $(1\bar{1}0)$ peak measured from the general background is described in Figure 2.4. Kaolinite with Hinckley index < 0.6 is considered as high-defect or poorly crystallized kaolinite. Low-defect kaolin has a high Hinckley index > 0.7 and is called well-ordered or well-crystallized kaolinite. Well crystallized kaolinite displays sharper X-Ray diffraction peaks than poorly crystallized kaolinite.

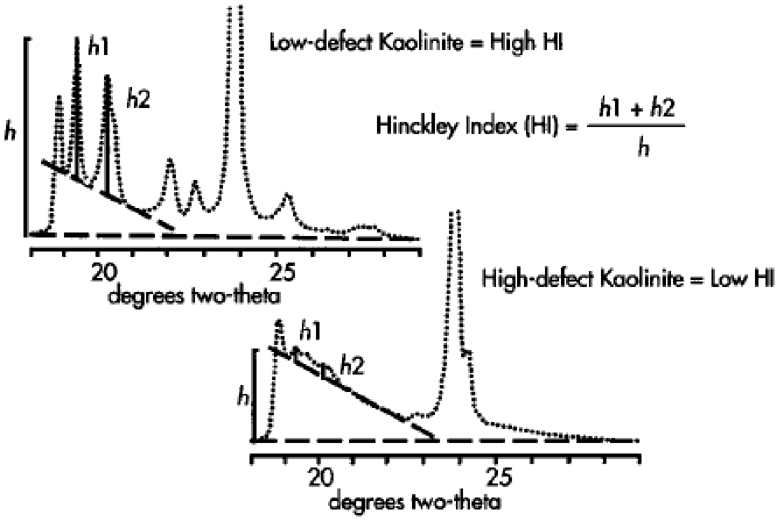

Figure 2.4: Method to compute Hinckley Index from X-Ray diffraction pattern of random oriented kaolin powder (Kogel et al., 2006). Peak at h1 and h2 is equivalent to the $(1\bar{1}0)$ and $(11\bar{1})$ peak respectively.

The textural property, or shape and size distribution of kaolin crystallites are important in its commercial uses, as they can directly affect the physical behaviour of clay (Bates, 1963). In the production of whiteware, clay is used as binder which provides plasticity in a body, and this property is determined by the particle size distribution and crystal morphology of clay (Carty & Senapati, 1998). Fine and platy kaolinite tend to impart plasticity better than coarse kaolinite booklets, as the clay particles finer than 2 μm are the major material responsible for the plastic behaviour (Ryan & Radford, 1987). For application as coating agent or functional filler, commercial specifications for the physical properties of kaolin products are standard (Kogel et al., 2006). Platy kaolin with fine and uniform particle size is desired to provide gloss, brightness, opacity and smooth surface in paper and paint coating

(Jepson, 1984). Filler grade kaolin on the other hand is more tolerable on the particle size requirements. Table 2.2 shows the requirement on particle size distribution and some other specifications for kaolin products to be used in above discussed applications.

Table: 2.2 Some industrial specification on kaolin products for paper coating, paper filler and ceramics applications (Siddiqui, et al., 2005).

Application		Paper coating	Paper filler	Ceramics
Mineral composition	Kaolinite	93 – 99 %	90 – 95 %	-
	Mica	7 – 10 %	5 - 10 %	-
Elemental composition	SiO_2	45 – 47 %	46 – 48 %	48 – 49 %
	Al_2O_3	37 – 38 %	37 – 38 %	36.1 – 37 %
	Fe_2O_3	0.5 - 1.0 %	0.5 - 1.0 %	0.6 - 1.0 %
	TiO_2	0.5 - 1.3 %	0.04 - 1.5 %	0.02 - 0.10 %
	Losses on Ignition	13.9 - 14.3 %	12.3 - 13.7 %	11.2 - 12.5 %
Particle size distribution	$<2\mu m$	89 – 92 %	60 – 80 %	40 – 70 %
	$<10\mu m$	100 %	85 – 97 %	80 – 96 %
	$<63\mu m$	-	-	100 %
Brightness		90 - 92	82 - 85	75 - 90

2.6 Physical properties of kaolin

2.6.1 Plasticity

Plasticity is defined as the property of a material which permits it to be deformed under stress without rupturing and to retain the shape produced after the stress is removed (Grim, 1968). Plasticity of clay is related to the morphology of the plate-like clay mineral particles that slide over the others when water is added, which acts as a lubricant, and presence of organic matter can also improve the plasticity of clay (Bergaya et al., 2006). In the plastic forming method, green body of ceramic are shaped