CHARACTERIZATION OF CAMBODIAN CLAYS AND THEIR SUITABILITY FOR CERAMIC TILES APPLICATIONS

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CHARACTERIZATION OF CAMBODIAN CLAYS AND THEIR SUITABILITY FOR CERAMIC TILES APPLICATIONS

by

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BUN KIM NGUN

TABLE OF CONTENTS

CHAPTER 1 – INTRODUCTION

CHAPTER 2 – LATERATURE REVIEWS

CHAPTER 3 – MATERIALS AND METHODOLOGY

CHAPTER 4 – RESULTS AND DISCUSSION

CHAPTER 5 – CONCLUSION AND RECOMMENDATION

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

a*	:	Degree of reddish
b*	:	Degree of yellowish
BBC	:	Clay is taken from Batang Berjuntai, Selangor, Malaysia
BET	:	Brunauer-Emmett-Teller
C1, C2 and C3	:	Clays were taken from Kamporng Chhnang, Cambodia
C4	:	Clay was taken from Kandal, Cambodia
CEC	:	Cation exchange capacity
DOE	:	Design of experiment
DTA	:	Differential Thermal Anaysis
ICCD	:	International Center for Diffraction Data
L*	:	Degree of lightness
LFS	:	Linear firing shrinkage
LL	:	Liquid limit
LOI	:	Loss on ignition
MOR	:	Modulus of rupture
O	:	Octahedral sheet
PDF	:	Powder Diffraction File
PI	:	Plastic index
PL	:	Plastic limit
R^2	:	Coefficient of multiple determination
R_A^2	:	Adjusted coefficient of determination
RMSE	:	Root mean square error

S_{BET} : Specific surface area

SEM : Scanning electron microscopy

T : Tetrahedral sheet

TG : Thermogravimetric analysis

TOC : Total organic content

WA : Water absorption

XRD : X-ray Diffraction

XRF : X-Ray Fluorescence

ΔE^* : Color differences

PENCIRIAN TANAH LIAT KEMBOJA DAN KESESUAIANNYA UNTUK APLIKASI JUBIN SERAMIK

ABSTRAK

Kajian yang dijalankan adalah bertujuan untuk memberikan data saintifik yang lebih mendalam tentang pencirian tanah liat Kemboja dan kesesuaiannya bagi aplikasi jubin seramik. Kajian ini meliputi tiga bahagian – Bahagian I adalah berkaitan dengan pencirian sifat-sifat sampel tanah liat mentah, Bahagian II adalah penyelidikan ke atas perubahan sifat-sifat antara tanah liat pukal dan pecahan tanah liat (<2 μm) dan Bahagian III adalah berkaitan dengan pengoptimumam komposisi jubin seramik yang mengandungi tanah liat Kemboja dengan menggunakan teknik rekabentuk statistik. Dalam Bahagian I, sampel tanah liat dicirikan dari sudut sifat-sifat fizikal (taburan saiz partikel, kapasiti perubahan-semula kation, dan had-had keseragaman), komposisi kimia, analisis mineral, sifat terma dan ciri-ciri pembakaran. Kebanyakan data-data ini diplotkan dalam rajah-rajah rujukan untuk menilai kesesuaian tanah liat Kemboja bagi pelbagai aplikasi seramik. Dalam Bahagian II, sampel-sampel tanah liat pukal dan kelompok pecahan tanah liat dicirikan melalui sifat-sifat fizikal, komposisi kimia, warna jasad seramik selepas pembakaran, perubahan fasa selepas pembakaran, mikrostruktur jasad seramik dan hubungkaitnya dengan ciri-ciri pembakaran. Akhirnya dalam Bahagian III, sampel-sampel tanah liat yang terpilih telah dicampur dengan feldspar dan silika komersial untuk menghasilkan jasad jubin. Sepuluh formulasi telah direkabentuk menggunakan kaedah campuran eksperimen. Model regresi yang berkaitan dengan pengecutan bakar linear (LFS), penyerapan air (WA) dan modulus pecah (MOR) telah dihasilkan dan dianalisis. Keputusan menunjukkan tanah liat Kemboja yang dikaji memberikan kelakuan plastik yang tinggi. 3 oksida utama seperti SiO_2 (51 – 57 %), Al_2O_3 ($\approx$ 22 %) dan Fe_2O_3 (5 – 11 %) telah ditemui dalam sampel-sampel tanah liat tersebut. Puncak-puncak utama dari analisis mineral menandakan wujudnya kuarza, lapisan klorit-vermikulit, ilit and kaolinit. Rajah-rajah yang dihasilkan menunjukkan tanah liat Kemboja adalah lebih sesuai bagi seramik struktur. Sampel-sampel kelompok pecahan tanah liat menunjukkan peningkatan nilai spesifik luas permukaan partikel (S_{BET}) dan kapasiti penukaran kation (CEC). Terdapat perubahan dalam kandungan oksida dalam sampel-sampel tanah liat pukal dan kelompok pecahan tanah liat. Oksida-oksida Al_2O_3, K_2O, CaO and MgO menunjukkan peningkatan dalam kelompok pecahan tanah liat, manakala oksida-oksida SiO_2 dan Fe_2O_3 pula menunjukkan pengurangan. Pembakaran pada suhu $\geq$ 1050 ^{o}C menyebabkan pembentukan fasa-fasa baru seperti mulit dan hematit dalam kesemua sampel dan hanya fasa kristobalit bagi sampel C1. Pemerhatian mikrostruktur dan data pencirian pembakaran menunjukkan suhu pembakaran pada 1050 ^{o}C merupakan suhu pembakaran minimum bagi tanah liat Kemboja. Daripada analisis satatistik, komposisi campuran yang optimum bagi jasad jubin seramik yang mengandungi tanah liat Kemboja (C1 dan C4) telah memenuhi keperluan spesifikasi piawai. Kajian ini telah membuktikan bahawa tanah liat Kemboja sesuai sebagai bahan mentah bagi penghasilan jubin seramik.

CHARACTERIZATION OF CAMBODIAN CLAYS AND THEIR SUITABILITY FOR CERAMIC TILES APPLICATIONS

ABSTRACT

The present work is aimed to provide detail scientific data on characterization of Cambodian clays and their suitability for ceramic tiles applications. The study covered three parts – Part I deals with characterization of the properties of the raw clay samples, Part II deals with investigation on changes of the properties between bulk and clay fraction (< 2 μm), and Part III deals with optimization of ceramic tile compositions incorporating Cambodian clays by using statistical design technique. In Part I, the raw clay samples were characterized in terms of physical properties (particle size distribution, cation exchange capacity, consistency limits), chemical composition, mineralogical analysis, thermal property, and firing characteristics. Some of these data were plotted on the reference diagrams to evaluate the suitability of the Cambodian clays for various ceramic applications. In Part II, the bulk and clay fraction samples were characterized on their physical properties chemical composition, color of ceramic body after firing, transformation of phases after firing, microstructure of ceramic bodies, and relationships within the firing characteristics. Finally in Part III, the selected clay samples were mixed with the commercial feldspar and silica to formulate the tile body. Ten formulations were designed by using mixture experiment methodology. Regression models related to linear firing shrinkage (LFS), water absorption (WA) and modulus of rupture (MOR) were generated and analyzed. Results showed that the studied Cambodian clays present very high plastic behavior. There major oxides such as SiO_2 (51 – 57 %), Al_2O_3 (≈

22 %) and Fe_2O_3 (5 – 11 %) were observed in the clay samples. The main peaks from the mineralogical analysis were assigned to quartz, chlorite-vermiculite mixed-layer, illite and kaolinite. The evaluation diagrams illustrated that the Cambodian clays are most suitable for structural ceramics. The clay fraction samples showed the improvement of the specific surface area (S_{BET}) and cation exchange capacity (CEC). values. Differences of oxides contents were found between the bulk and clay fraction samples. The oxides showing increment in the clay fractions are Al_2O_3, K_2O, CaO and MgO, whereas those showing decrement are SiO_2 and Fe_2O_3. Firing at ≥ 1050 ^{o}C led to the formation of new phases such as mullite and hematite for all the samples, and cristobalite for C1. Judging from the microstructure and firing characteristic data, firing temperature of 1050 ^{o}C is considered as the minimum for Cambodian clays. From the statistical analysis, the optimum mixture compositions for ceramic tile bodies incorporating Cambodian clays (C1 and C4) to meet the requirements of standard specifications were obtained. This study proves that the Cambodian clays are suitable as raw materials for the production of ceramic tiles.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The term “clay” refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Reeves et al., 2006). Clays are ubiquitous constituents of the earth’s crust and are one of the most abundant minerals found near the earth’s surface that serve as raw materials for traditional ceramics. Clay has been known and used by human being since the ancient time (Grim, 1968). Moreover, clays are by far very important in industries, agriculture, engineering, construction, geology, environmental, and miscellaneous applications (Lee and Yeh, 2008; Mahmoudi et al., 2008).

It is still true that clays are, by far, the raw material most extensively used in the manufacturing of ceramic articles, such as porcelains, pottery wares, and sanitary wares. Indeed, they have been widely used as the main raw materials in the fabrication of diversified ceramic products for construction materials such as bricks and tiles due to many of their specific properties before and after firing (Murray, 2007; Lee and Yeh, 2008; Mahmoudi et al., 2008). The properties of clay that are of interest to the ceramics industry are its plasticity which facilitates the shape of the body, particle size distribution, chemical composition, mineral composition, thermal property, color, refractoriness, and mechanical strength after firing (Burst, 1991; Baccour et al., 2009). Each of the properties has inter-influence to the others, i.e. the particle size distribution (especially clay fraction content) has been reported to affect the plasticity, cation exchange capacity and also mechanical strength (Grim, 1968; Bergaya et al., 2006; Reeves et al., 2006). Chemical composition, i.e. Fe_2O_3, has reported to influence significantly on the color of the ceramic body. With increase of Fe_2O_3 content, the reddish color of ceramic body becomes stronger (Das et al., 2005; Kara et al., 2006). Moreover, Baccour et al. (2008) and Jordán et al. (2009) reported that the clay's mineral phases and mineral composition play a great influence to the fired properties. Therefore, the requirements to fully understand of the above-mentioned clay properties become very essential. This is the basic of optimization of a clay usage in various traditional ceramic products.

The final stage in clay ceramic processing, except for a few cases such as that of sun-dried adobe bricks, is firing at a high temperature (generally above 900 ^{o}C). Firing is considered the most influential factor in ceramic manufacturers. Mota et al. (2008) stated that firing property plays a significant role in the quality control of final products. In the firing of clay, when temperature is above 900 ^{o}C, glassy phase and liquid phase occurred due to the presence of alkaline earth oxides, mainly K_2O and Na_2O. These oxides, in reaction with silica and alumina, promote liquid phase formations that facilitate densification. Hence, temperature of 900 or 950 ^{o}C are conventionally taken for granted as being the minimum for clay ceramic firing (Monteiro and Vieira, 2004; Lee and Yeh, 2008; Baccour et al., 2009).

Natural clays are low-cost and readily available materials functioning as excellent plastic behavior for ceramic body forming. Due to inherently complex physical, chemical and mineralogical characteristics, clays usually have unique properties related to their own natural diagenesis. For economic reasons, the ceramic industry for building materials, therefore, has to use clays from nearby deposits. As a consequence, the characterization and quality control of each clay is important for the technical performance of local products. Moreover, a specific deposit may have distinct layers associated with different clays. This gives a local industry the opportunity to mix different clays in order to adjust the properties of both the unfired ceramic body and corresponding final product (Bergaya et al., 2006; Vieira et al., 2008). For this reason, special attention should be paid to investigate the possibilities of using local Cambodian clays for the production of building materials such as bricks and tiles (wall, floor and roofing). At present, many traditional ceramics have been manufactured from mixtures of different raw materials, which are shaped by casting, extrusion or compaction and fired at high temperature, to fulfill the product specifications. Those ceramics are generally bricks, dinner wares, sanitary wares, and roofing and floor tiles.

Bricks and tiles are very important ceramic materials and are widely used for civil constructions, especially for housing. There is a preferable economic point of view if these materials can be made locally. Ceramic tiles used for walls and floors are a type of structural ceramics and are a multicomponent system consisting of clay, quartz and carbonates, making them one of the most complex ceramic materials (Sousa and Holanda, 2005). In the process of tile fabrication, all raw materials are mixed together according to a specific design in order to fulfill desired properties. Therefore, each component, as well as its amount within the body, contributes differently to the final product (Sousa and Holanda, 2005; Alcântara et al., 2008). Generally, three components are used and play fundamental roles in optimizing the performance of the final properties of ceramic tiles. Clay is the first component, whereby its plasticity facilitates the shape of the body, while second is feldspar which is used for fluxing and the third is silica which is used as a filler and stabilizer material (Bender and Händle, 1982; Kamseu et al., 2007; Baccour et al., 2009). Besides these components, the final properties of ceramics are also influenced by other conditions in the production operations such as shaping, drying, firing temperature, and thermal gradient, etc. Firing profile plays an immense role in adjusting of the final properties of the tiles, normally through liquid-phase formation (Alcântara et al., 2008; Lee and Yeh, 2008). In the industrial processing of ceramic bodies such as floor and wall tiles, linear firing shrinkage (LFS), water absorption (WA), and modulus of rupture (MOR) have been reported to be important factors in judging the quality and process control in the development and manufacturing states (Correia et al., 2004a; b).

Clay materials are generally influenced by climatic conditions, weathering intensities, and source of the parent rocks (Bender and Händle, 1982); therefore the properties of different clays are not the same. Prior to making the decision to use any local clay deposit in the production of industrial ceramic tiles, especially clay deposits in Cambodia which has never been investigated before, a series of trial experiments and evaluation is mandatory. In general practice, the evaluation results from the first trial batch can be used as the basis or starting point from which further adjustment of the mixture’s proportions and testing can be made until the required properties are achieved. However, this conventional method for optimization of the performance of the ceramics is time consuming and may not be able to reveal the real optimum composition. Therefore, a statistical design methodology specific to mixture design experiments is becoming a common practice technique in order to both achieve desired properties and to establish an optimized mixture for a given constraint with minimum experimental numbers (Nardi et al., 2004; Menezes et al., 2008; Lassinantti Gualtieri et al., 2011).

Investigation on the properties of Cambodian clays could open a huge window opportunities to the manufactures for setting up of a variable clay-based ceramic making industries with lower cost and better quality.

1.2 Geological setting of the studied areas

Clays are distributed widely in almost all parts of Cambodia (Figure 1.1). They are divided into two groups of clay deposits of the central alluvial plains (the Tonle Sap plain and the Mekong plain) and those formed by the deep weathering and alteration of parent igneous rocks, usually granitic or rhyolitic rocks (Cambodia, 1993). Figure 1.2 shows the geological map of the studied areas and its surrounding. It covers the geological information of the major clay deposits of Kampong Chhnang and Kandal. The current eluvial clay deposit in Kampong Chhnang originated from the weathering and alteration of Late Jurassic-Cretaceous granite (high land area) to old alluvium, which was further altered and transported to the recent alluvium. Altered basaltic volcanic rocks are predominant sources besides granitic rocks for this formation. This clay deposit was also influenced by the Tonle Sap plain since its location is very close to the Tonle Sap plain and moreover the volume of the Tonle Sap plain is evaluated to be four times larger during the rainy season. By contrast, the Kandal clay is a recent deposit derived from the Tonle Sap and the Mekong plains, especially much influenced from the Mekong plain as illustrated in Figures 1.1-1.2. These clay deposits were found in open quarries.

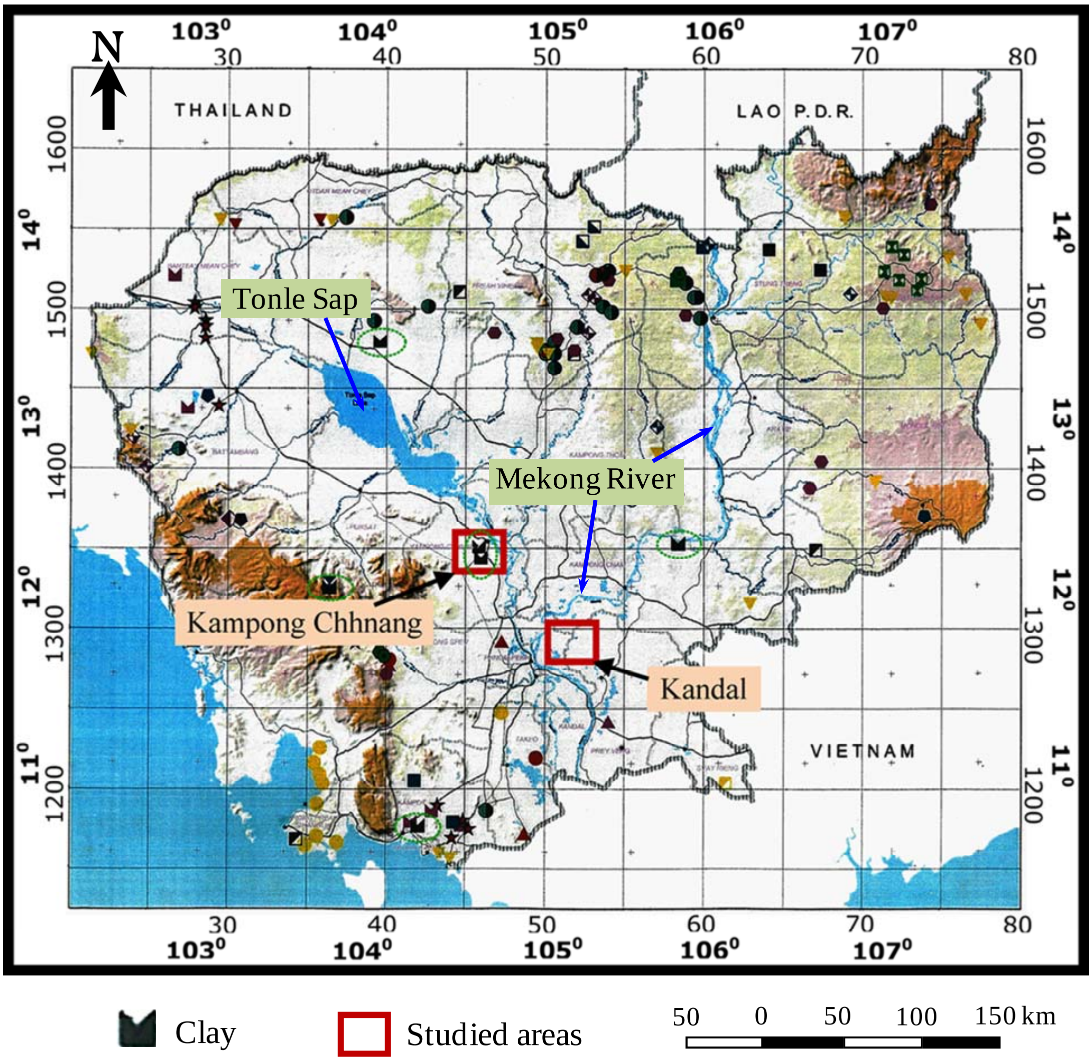

Figure 1.1: Mineral resources map of Cambodia (MIME, 1998)

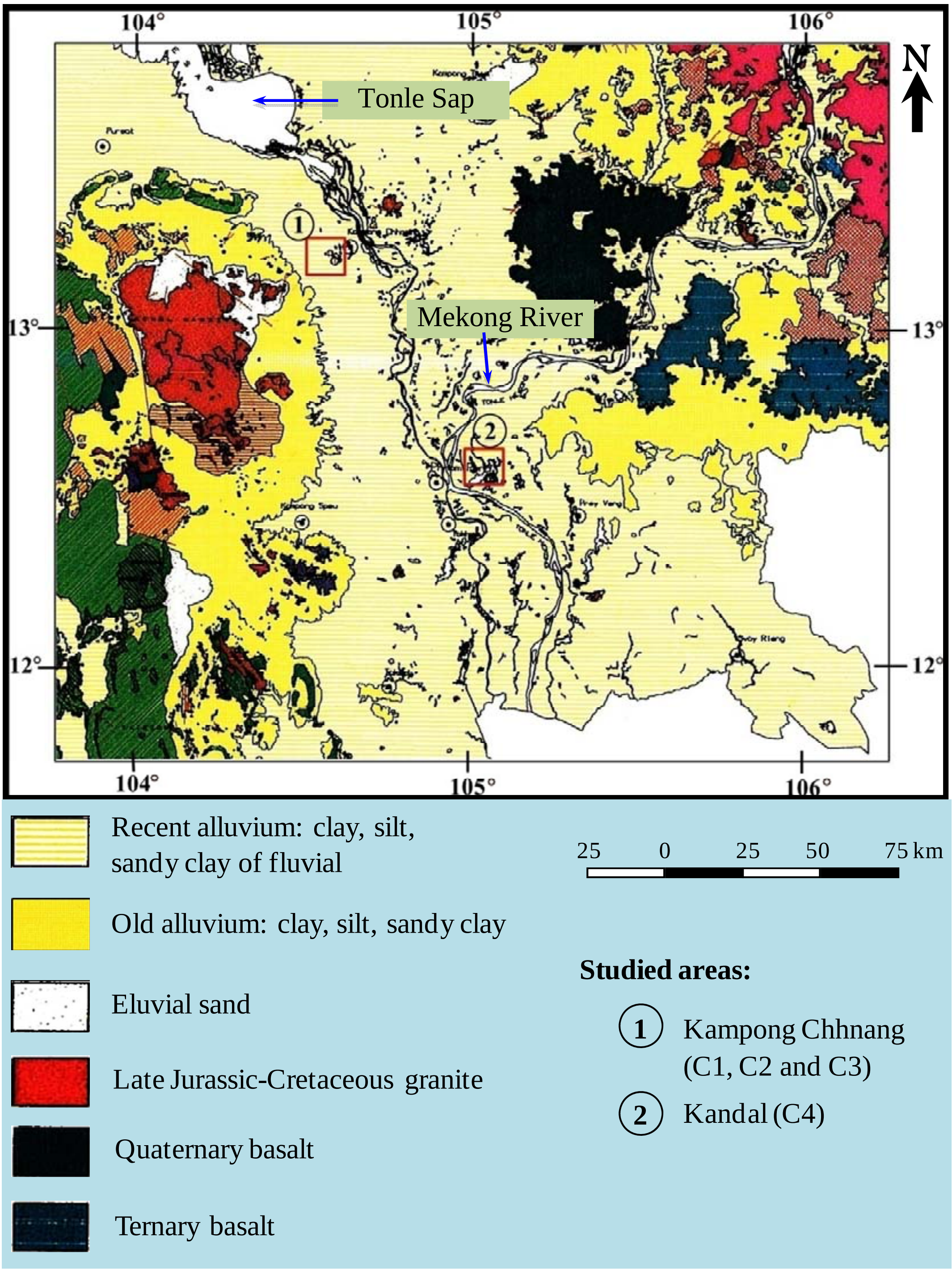

Figure 1.2 Geological map of the studied and surrounding areas (MIME, 1998)

1.3 Problem statement

Worldwide, clays are the main raw materials exploited in the fabrication of diversified building ceramic products such as bricks and tiles. From economic point of view, as mentioned earlier, the local clay deposits are the most preferable use in those productions. Table 1.1 summaries the references from previous research works which used local clays for the production of building materials in various parts of the world. Since Cambodia has lots of potential clay deposits, it is timely for this country to start the production of local-made building materials.

Table 1.1: The literature on using local clay deposits for structural ceramics from various parts of the world

Authors	Country	Year of publication
Tracey-White	Indonesia	1980
Fiori et al.	Italy	1989
Nyakairu et al.	Uganda	2002
Saikia et al.	India	2003
Lingling et al.	China	2005
Freyburg and Schwarz	Germany	2007
Jordan et al.	Spain	2008
Mahmoudi et al.	Tunisia	2008
Türkmenoglu and Yavus-Isik	Turkey	2008
Vieira et al.	Brazil	2008
Andji et al.	Ivory Coast	2009
Loryuenyoung et al.	Thailand	2009
Wattanasiriwech et al.	Malaysia	2009
Pardo et al.	Chile	2011

Cambodia is a Southeast Asian country with an abundance of natural resources especially clays which can be found in almost all parts of the country. These clays have, however, been used as raw materials for ceramic products since 9th century (during Angkor period (802 – 1431)). Moreover, few Khmer ceramics were found from the pre- and post-Angkorian periods by the archaeological evidence in its own history (Rooney, 1984). Currently, there are still hundreds of small traditional pottery factories having used local clays throughout the country. Simple techniques for making potteries and other wares have been traditionally used based on the experience of potters, even though the properties of raw materials are not well understood.

Cambodia's clay-based ceramics have faced economic challenges for people's daily lives. As the report of the Icon Group (Icon Group, 2002) - the worldwide market potential for clay, ceramic and refractory minerals of Cambodia, Cambodia earned about US$ 1 million each year from 1995 to 2005. This amount was shown very much lower compared to the neighbors e.g. Vietnam made average about US$ 6.2 millions, Thailand about US$ 36.8 millions, Malaysia about US$ 20.1 millions, and Indonesia about US$ 43.3 millions.

Clay deposits have an important economic potential in the municipality, where the raw materials for industrial applications like ceramic productions, mainly bricks and roof tiles is plentiful. Potential sources of clay materials for ceramic applications was discovered in central region of Cambodia, namely Kampong Chhnang and Kandal (Figure 1.1). Kampong Chhnang clay deposits are mainly being used for potteries, dinner and kitchen wares, and ceramic souvenirs, whereas, Kandal clay deposits are being widely used for red bricks by local ceramic industries. However, the quality of these ceramics is often poor, in particular, there is lack of manpower skilled and experienced, and also lack of scientific researches and knowledge on the behavior of raw clay materials. Beside bricks, other construction materials such as roofing tile, wall and floor tiles, most of them are imported from

China, Indonesia, Thailand, Spain, Italy, and other countries. As a consequence, tiles are expensive for the population. Nevertheless, no study was devoted to the tiles made by local clays. In recent years, there has been an increase in construction activities in Phnom Penh (capital city of Cambodia). Therefore, the above-mentioned ceramic products cannot meet the ever-increasing market demand for the construction materials needed. Traditional methods of the ceramic production, which do not take into account chemical and mineralogical characteristics, are still being widely practiced in Cambodia.

To optimize the potential use of local raw materials such clays for various ceramic productions, researches on each deposit of those materials should be carried out. Cambodian clays, unfortunately, have not been clearly characterized in detailed according to their mineralogical, chemical, and firing properties. No or little studies on the quality and potential use of Cambodian clays have been carried out, although clay is a primary material for local ceramic manufacturers (Rooney, 1984; Cambodia, 1993). The knowledge of origin, physicochemical composition, and firing properties of the clays is essential when designing their suitable use for the ceramic production. These characteristics can help for best exploitation and eventually may open up new areas of application (Baccour et al., 2008; Jordan et al., 2008). For this reason, particular attention should be paid to begin the investigation of some clay deposits in Cambodia which can provide both academic value and immediate commercial importance.

1.4 Objective

The main objectives of this study are:

- To provide scientific data of various Cambodian clay deposits.
- To understand the behaviors of the clays and clay minerals in both unfired and fired states.
- To highlight the potentiality and suitability of using Cambodian clays in the fabrication of ceramic tiles using statistical approach.

1.5 Scope of research

To achieve the above mentioned objectives, research experimental investigations were divided into three main parts as follow:

Experimental

Part I: To characterize the Cambodian raw clay samples (natural state) on their physical, chemical, mineralogical, thermal, dry bending strength, and firing properties. To determine the firing properties, the samples were fired for 1 h at 800, 900, 1000, 1100, and 1200 ^{o}C, respectively.

Part II: To characterize the clay fraction (particle size < 2 µm) samples (clay fraction was collected from the bulk sample by repeated sedimentation method) on their physical, chemical, mineralogical, ceramic body color, and firing properties. To determine the ceramic color and firing properties, the samples were fired for 1 h at 950, 1000, 1050, 1100, and 1200 ^{o}C, respectively. In this part, the properties of bulk clay samples (Cambodian clays) and a Malaysian clay (BBC) were used for comparison. BBC clay is a natural clay which was originally taken from Batang Berjuntai, Selangor, Malaysia.

Part III: To characterize the properties of clay samples on laboratory and industrial scales of ceramic tiles application. In this part, 10 mixes (clay + feldspar + quartz), with different amount of each component, were prepared according to the standard of the ceramic tile procedures (wet grinding, drying, granulation, moisturizing, uniaxial pressing, and firing). The tile bodies were fired at 1170 ^{o}C and tested on firing shrinkage, water absorption, and flexural strength. Statistical design of mixture experiments was used to optimize the suitable mixtures according to the standard desired tile properties.

CHAPTER 2

LITERATURE REVIEW

2.1 History of clay-based ceramics in Cambodia: from the past to the present

The influence of Khmer culture and architecture inside and outside of Cambodia are indicative on how widespread Cambodia’s domination was in Southeast Asia. It is true that history of Khmer ceramics lies on the civilization and evolution of the Cambodian history. The history of Khmer (known as Cambodia today) civilization has largely been recorded in the inscriptions which adorn the monumental temple complexes. The temple architecture and the related sculptural traditions showed the development and modernity of the Khmer Empire – the empire during Angkorian period from 9th to 15th centuries and the most prosperous and powerful kingdom in Southeast Asia (Guy, 1989; Gin, 2004). In the Angkorian period, Angkor Wat temple (Figure 2.1) was built at the height of political power of the reign of King Sūryavarman II (r. 1113-ca. 1150) for his state temple and capital city. It was claimed the first large-scale stone Khmer temple structure which illustrated one of the most beautiful examples of the Khmer art. The temple has been smiling for more than 800 years now.

Angkor Wat, however, was not the only temple constructed during the reign of the King Sūryavarman (Guy, 1989; Gin, 2004; Rooney, 2005). Khmer artisan potters were, however, developing highly sophisticated ceramics whose individuality in form and decoration clearly sets them apart from those of other countries in Asia. The development of Khmer ceramic art, beginning in the Angkorian period, can be found in the carved stone and on the walls and pediments of Prah Vihar (dating from the 11th century), Angkor Wat (first half of the 12th century), the Bayon (12th century), and Banteay Chmar (12th century) (Frasché, 1976).

Figure 2.1: Angkor Wat Temple of Cambodia (Culturefocus.com)

The monument of Angkor Wat was made out of enormous amounts of sandstone and some of laterite was used for the outer wall and for hidden structural parts. This sandstone was claimed to be transported from Mount Kulen (or Phnom Kulen). It was believed that Phnom Kulen is not just the place for supplying the main materials for Angkor Wat construction, but it is also the place where other activities can be found, e.g. discovery of Khmer ceramics. Little excavation work has been undertaken which could provide reliable information to understand the Khmer ceramic tradition and its evolution (Guy, 1989). At least some Khmer potteries, and perhaps most of them, were manufactured on the hill called Phnom Kulen, 40 kilometers north-east of Angkor and with approximation 8-10 km by 20 km in area. During that time, no detailed examination of the kiln-site has been made; however, the manufacture continued over at least three centuries after the establishment of the Khmer dynasty at the Phnom Kulen by Jayavarman II in 802 A.D., and it is perhaps the place where the earliest Khmer kilns producing glazed pottery appear to be located (Willetts, 1971; Brown, 1988). By the study of Khmer art history, the term 'Kulen' is applied to a specific architectural style of ceramics at the ninth century, a style found on Phnom Kulen. The style had been made at the site for a full 400 years, from the late 9th to the late 13th centuries. Generally, the term has been used for referring to all yellowish- to greenish-glazed Khmer ceramics (Brown, 1988).

As reported by Willetts (1971), the majority of pots which were displayed in the Museum Exhibition belonged to either the Sukhothai or Sawankoloke kilns of Thailand or the kilns of North Vietnam. Those pots were made either to the 14th or the 15th centuries, so that they are about five and six hundred years old. However, the earliest wares on the display were made from the 11th to the 13th centuries, are undoubtedly called '*Khmer ceramics*', and which were produced in Cambodia as illustrated in Figures 2.2-2.3.

The development of ceramic industries in Cambodian today is very limited compared to other countries in Southeast Asia, though there are potential natural resources, e.g. clays. Such clays are very limited used for ceramic applications. For example, clay deposits in Kampong Chhnang are the main clay resources being used for the pottery, dinner and kitchen wares, and other ceramic products (Figures 2.4-2.5). Other clay deposits in Kandal are also important resources for ceramic

Figure 2.2: Khmer stonewares (left: vase, 11th – 13th century; right: jar, 11th – 13th century) (Frasché, 1976)

Figure 2.3: Khmer stonewares (left: oil jar, 11th – 13th century; right: bowl, 11th – 13th century) (Frasché, 1976)

production and mainly for bricks (Figure 2.6). These bricks are widely used for civil constructions especially supplies in the capital city. The above-mentioned factories cannot meet the ever-increasing market demand for the construction materials needed. Traditional methods of the ceramic production, which do not take into account chemical and mineralogical characteristics, are still being practiced in Cambodia.

Figure 2.4: Potteries and other ceramic products traditionally made in Kampong Chhnang

Figure 2.5: Ceramic water filter made in Kampong Chhnang

Figure 2.6: Procedures of making bricks in Kandal: (a) raw clay; (b) drying of extruded green body; (c) firing kiln and (d) fired bricks

Icon Group (2002) reported that the market potential for clay, ceramic and refractory minerals of Asia shares about 21.6% of the world market (Figure 2.7).

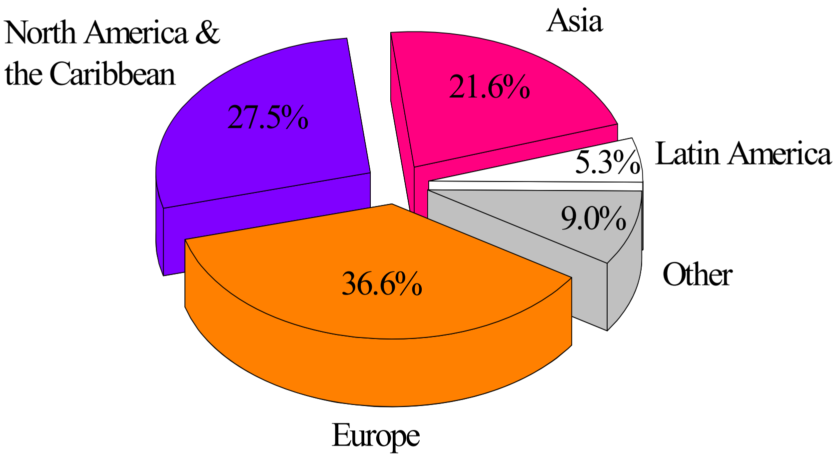

Figure 2.7: Worldwide Market Potential for Clay, ceramic and refractory minerals (US $ mln): 2000 (Icon Group, 2002)

Comparison of the market for clay, ceramic and refractory minerals within Asian countries is made and shown in Table 2.1. It can be seen that Cambodia earned about US$ 1 million each year from 1995 to 2005. This amount is very little compared to the other countries.

Table 2.1: The market for clay, ceramic and refractory minerals in Asian countries from 1995 to 2005 (US $ million) (Icon Group, 2002)

Year	Cambodia	China	Indonesia	Malaysia	Thailand	Vietnam
1995	1	175	45	21	38	6
1996	1	168	43	20	37	6
1997	1	163	42	20	36	6
1998	1	158	41	19	35	6
1999	1	153	41	18	34	6
2000	1	150	40	18	33	6
2001	1	156	41	19	35	6
2002	1	165	43	20	37	6
2003	1	174	45	21	38	6
2004	1	183	47	22	40	7
2005	1	193	49	23	42	7

Most of the Cambodian minerals such as clays are not yet characterized in detail in terms of their physical, chemical, mineralogical, and firing properties. These knowledge are very crucial for evaluating their potential suitability as raw materials in various ceramic applications. As it has been known that research and development discipline plays an important role in industrial civilization, product evolution, and economic development; therefore, particular attention should be paid to the investigation of clay deposits in Cambodia for ceramic industry applications.

2.2 Definition of clay and clay mineral

2.2.1 Clay

Until now, there is no uniform terminology yet for the word ***"clay"*** and ***"clay material"***. Their definition are given differently depends on the context in which they are being used; e.g. in geology, sedimentology, soil science, colloid science, etc. A summary definition by the joint nomenclature committees (JNCs) of the Association International pour l'Etude des Argile (AIPEA) and the Clay Minerals Society (CMS) defines that the term "clay" refers to a *naturally occurring* material composed primarily of *fine-grained* minerals, which is generally *plastic* at appropriate water contents and will *harden* when dried or fired. This definition is more appropriate for the field of ceramics. According to this definition, synthetic clays are not considered as clay even though they may be fine grained, and display the properties of plasticity and hardening on drying and firing (Bergaya et al., 2006; Reeves et al., 2006). Although clay usually contains phyllosilicates, it may contain also other materials such as non-clay mineral and organic matter which impart plasticity and harden when dried or fired. The JNCs stated that 'minerals known to produce the property of plasticity are phyllosilicates'.

Grim (1962) gave a definition to a "clay material" that it is any fine-grained, natural, earthy, argillaceous material. Furthermore, "clay" can be used in a rock term and also as a particle size term (a key parameter in all definition of clay). As a particle size term, the size fraction comprised of the smallest particles is called the 'clay fraction'. Different disciplines of scientists have conventionally limited a maximum size of clay particles. For pedologists, the term 'clay fraction' refers to a class of materials whose particles are smaller than 2 μm in equivalent diameter *(e.s.d.)*. For most geologists and soil scientists use particle less than 2 μm, sedimentologists and geoengineers use 4 μm, and colloid scientists use 1 μm for clay particle size (Bergaya et al., 2006; Reeves et al., 2006; Murray, 2007). In addition, base on the British Civil Engineering Practice, clay is defined as material of particle size less than 0.002 mm (Reeves et al., 2006). However, Wentworth's scale defines the clay grade as particle finer than 4 μm, which is used by many engineers and soil scientists whereas clay scientists consider 2 μm as the upper limit grade of the clay size as reported by Murray (2007).

2.2.2 Clay mineral

Unlike clay, the term ***"clay mineral"*** is difficult to define. At first, the term signifies approximately as a class of hydrated phyllosilicates making up the fine-grained fraction of rocks, sediments, and soils (Bergaya et al., 2006). According to the definition proposed by the JNCs, clay mineral refers to phyllosilicate minerals and minerals which impart plasticity to clay and which harden upon drying or firing. In this definition, the term is regardless to the grain size features. Because minerals are not defined based on their crystallite size, appropriate phyllosilicates of any grain size may be considered as "clay minerals", therefore, macroscopic mica such as vermiculite and chlorite may be regarded as clay mineral. In general sense to the JNCs's definition, clay mineral can be either natural or synthetic, phyllosilicates or non-phyllosilicates, and have no size restriction (Bergaya et al., 2006). Besides, Grim (1968) summarized what he termed the clay mineral which defined that clays are composed essentially of a small group of extremely small crystalline particles of one or more members of a group of minerals that are commonly known as the clay minerals. Murray (2007) stated that clay minerals are hydrous aluminum silicates.

Iron and magnesium generally substitute for the aluminum in some of those minerals and in some there are alkaline and alkaline earth presented as essential constituents. There are various groups of clay mineral such as kaolinite, smectite, illite, chlorite, vermiculite, and mixed-layered which will be discussed in detail in section 2.3.

2.2.3 Distinction between clay and clay mineral

The term ‘clay’ and ‘clay mineral’ has been used in various fields such as soil science, geology, and etc. It must always be kept in mind about the distinction between their terminologies. Again, the term clay can signify as a rock, a sedimentary deposit, and the alteration (weathering) products of primary silicate minerals. As the clay materials are formed from different origins, they usually result in different clay mineral constituents. Therefore, current name of clays can be given and summarized in Table 2.2. However, some literatures often use the term clay instead of clay mineral for shorter terminology. The distinct differences of clay and clay mineral are summarized in Table 2.3.

2.3 Structure of clay minerals

The clay minerals are a group of hydrous aluminosilicates that are characteristically found in the clay (< 2 μm) fractions of sediments and soils. Each of the clay minerals is composed of a unique combination of layers that are made up of either tetrahedral or octahedral structural units that form sheets (Reeves et al., 2006; Shackelford and Doremus, 2008). In each tetrahedron a silicon atom is equidistant from four oxygens or hydroxyls if needed to balance the structure, arranged in the form of a tetrahedron with a silicon atom at the center and the silica tetrahedral groups are arranged to form a hexagonal network (Figure 2.8a).

Table 2.2: Current names of clays (Bergaya et al., 2006)

Current name of clays	Origin	Main clay mineral constituents	Remark
Ball clay	Sedimentary	Kaolinite	High plasticity, white burning
Bentonite	Volcanic rock alteration or authigenic	Montmorillonite	
Bleaching earth	Acided-activated bentonite	Decomposed montmorillonite	
Common clay	Sedimentary or by weathering	Various, often illite/smectite mixed-layer mineral	General for ceramics Excluding porcelain
China clay	Hydrothermal	Kaolinite	Kaolinite from Cornwall plastic, white burning
Fire clay	Sedimentary	Kaolinite	Plastic, high refractoriness
Flint clay	Sedimentary with subsequent diagenesis	Kaolinite	Non-slaking, non-plastic, used for refractories
Fuller's earth	Sedimentary, residual, or hydrothermal	Montmorillonite, sometimes palygorskite, sepiolite	
Primary kaolinite	Residual or by hydrothermal alteration	Kaolinite	
Secondary kaolinite	Authigenic sedimentary	Kaolinite	
Refractory clay	Authigenic sedimentary	Kaolinite	With low level of iron, alkali and alkali earth cations for refractories
Laponite	Synthertic	Heetorite-type smectite	
Nanoclay		Mostly montmorillonite	Superfluous term for clays used for nanocomposites

Table 2.3: Summary of the distinction between clay and clay mineral (Bergaya et al., 2006)

Clay	Clay mineral
Natural	Natural or synthetic
Fine-grained (< 2 μm or < 4 μm)	No size criterion
Phyllosilicates as principle constituents	May include non-phyllosilicates
Plastic	Plastic
Hardens on drying or firing	Hardens on drying or firing

By sharing three of these oxygens between adjacent tetrahedra they may be linked together to form a continuous tetrahedral sheet (Figure 2.8b), in which the unshared oxygens all point in the same direction. Thus, one side of a tetrahedral sheet consists of an hexagonal network of shared oxygens, whilst the other side is formed by the remaining so-called apical oxygens. The octahedral sheet is comprised of closely packed oxygens and hydroxyls in which aluminum, iron, and magnesium atoms are arranged in octahedral coordination (Figure 2.9).

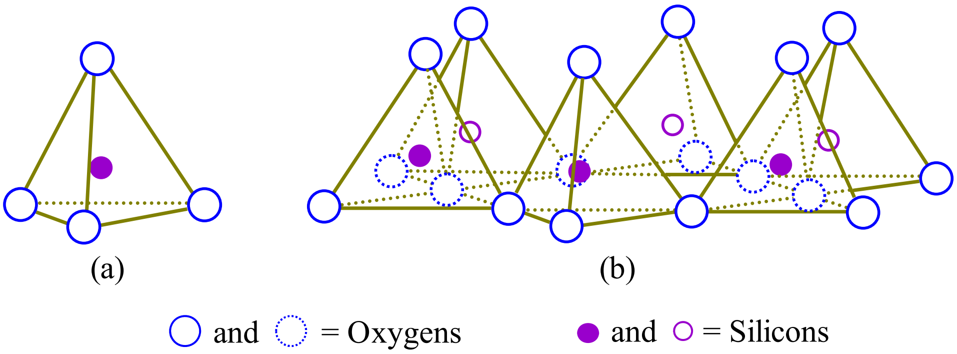

Figure 2.8: (a) a single Si–O tetrahedron and (b) the structure of the tetrahedral sheet (Murray, 2007)

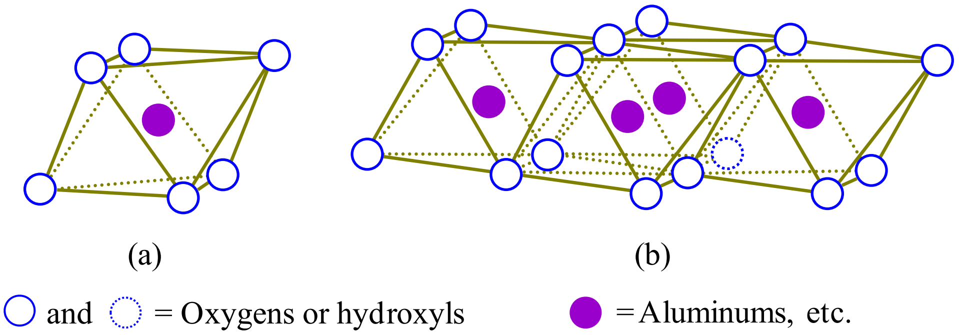

Figure 2.9: (a) a single Al–O octrahedron and (b) the structure of the octahedral sheet (Murray, 2007)

When aluminum with a positive valence of three is the cation present in the octahedral sheet, only two-thirds of the possible positions are filled in order to balance the charges. When only two-thirds of the positions are filled, the mineral is termed dioctahedral. When magnesium with a positive charge of two is present, all three positions are filled to balance the structure and the mineral is termed trioctahedral. Common tetrahedral cations are Si^{4+}, Al^{3+}, and Fe^{3+}, whereas octahedral cations are usually Al^{3+}, Fe^{3+}, Mg^{2+}, and Fe^{2+} (Grim, 1968; Middleton, 2003; Bergaya et al., 2006; Murray, 2007). By joining tetrahedral and octahedral sheets together, two basic clay mineral units known as layers can be formed. The unit formed by linking one tetrahedral sheet (T) and one octahedral sheet (O) together is called a 1:1 layer structure (T-O). The sheets are bonded together by the sharing of O^{2-} ions between the octahedral cation (Al^{3+}) and tetrahedral cation (Si^{4+}). The most common 1:1 mineral is dioctahedral (kaolinite). The 2:1 layer structure consists of one octahedral sheet sandwiched between two tetrahedral sheets (T-O-T) (Figure

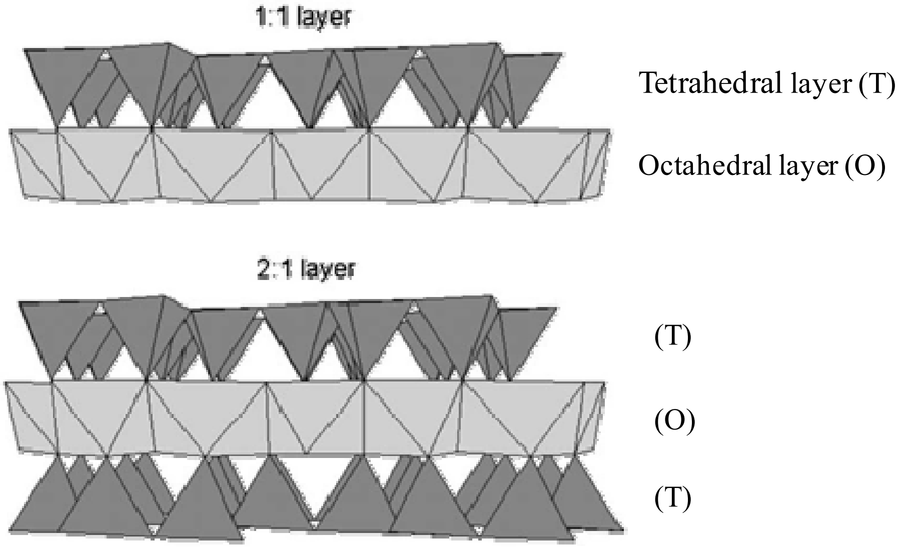

Figure 2.10: Models of composite layers in clay mineral structures (1:1 layer structure and 2:1 layer structure) (Bergaya et al., 2006)