การแยก การศึกษาและการดัดแปรแร่มอนต์โมริลโลไนต์ จากดินเหนียวในเขตจังหวัดนครราชสีมา ประเทศไทย

นางสาวณัฏฐิณี ศุภเมธานนท์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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SEPARATION, CHARACTERIZATION AND MODIFICATION OF MONTMORILLONITE IN CLAY FROM NAKHONRATCHASIMA PROVINCE, THAILAND

Miss Nuttinee Supamathanon

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SEPARATION, CHARACTERIZATION AND MODIFICATION OF MONTMORILLONITE IN CLAY FROM NAKHONRATCHASIMA PROVINCE, THAILAND

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

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ณัฏฐิณี ศุภเมธานนท์ : การแยก การศึกษาและการดัดแปรแร่มอนต์โมริลโลไนต์จากดินเหนียวในเขตจังหวัดนครราชสีมา ประเทศไทย (SEPARATION, CHARACTERIZATION AND MODIFICATION OF MONTMORILLONITE IN CLAY FROM NAKHONRATCHASIMA PROVINCE, THAILAND) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.ตริตาภรณ์ ชูศรี, 126 หน้า. ISBN 974-533-439-1

ได้มีการแยก การศึกษาและการดัดแปรแร่มอนต์โมริลโลไนต์จากดินเหนียวในเขตจังหวัดนครราชสีมา ผลการวิเคราะห์โดยเทคนิค XRD และ FTIR ยืนยันว่าแร่ดินเหนียวหลักที่มีอยู่ในอนุภาคดินเหนียวขนาดเล็กกว่า 0.2 ไมโครเมตร คือแร่มอนต์โมริลโลไนต์ แร่ที่มีปริมาณปานกลางคือเคโอลิไนต์ อิลไลต์ และแร่ผสมมอนต์โมริลโลไนต์-อิลไลต์ ส่วนควอร์ตซ์มีอยู่ในปริมาณน้อยถึงน้อยมาก ($\leq 2\%$) ได้เก็บตัวอย่างดิน 21 ตัวอย่างจากดินเวอร์ติโซล ซึ่งมีแร่มอนต์โมริลโลไนต์อยู่ในปริมาณสูง จากอำเภอเมือง อำเภอพิมาย และอำเภอโชคชัย ก่อนการแยกอนุภาคดินเหนียวจากดินจำเป็นต้องกำจัดคาร์บอเนต และอินทรีย์วัตถุเสียก่อน หลังจากกำจัดออกไซด์ของเหล็กแล้วได้ใช้เทคนิคการเลี้ยวเบนเลเซอร์ ศึกษาการกระจายตัวของอนุภาค พบว่าดินตัวอย่างทุกตัวอย่างมีอนุภาคดินเหนียว (เส้นผ่านศูนย์กลาง < 2 ไมโครเมตร) อยู่ในช่วง 28.51-73.63% ได้แยกอนุภาคดินเหนียวขนาดเล็กกว่า 0.2 ไมโครเมตร ซึ่งจะมีแร่มอนต์โมริลโลไนต์อยู่ในเปอร์เซ็นต์สูงโดยใช้กระบวนการเซนตริฟิวจ์ ได้ศึกษาอนุภาคดินเหนียวขนาดเล็กกว่า 0.2 ไมโครเมตรที่อิ่มตัวด้วยไอออนโซเดียม ด้วยเทคนิคการเลี้ยวเบนรังสีเอกซ์ (XRD) เพื่อดูค่า d-spacing, เทคนิคเอกซ์เรย์ฟลูออเรสเซนซ์ (XRF) เพื่อศึกษาส่วนประกอบทางเคมี กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) เพื่อศึกษาสัณฐานวิทยา เทคนิคฟูริเยร์อินฟราเรดสเปกโทรสโกปี (FTIR) เพื่อศึกษาข้อมูลเกี่ยวกับโครงสร้าง การใช้เทคนิคทางความร้อนคือ เทอร์โมแกรวิเมตริกอนาไลซิส (TGA) และดิฟเฟอเรนเชียลเทอร์มัลอนาไลซิส (DTA) เพื่อศึกษาสมบัติเชิงความร้อน ผลการศึกษาเทียบเคียงได้กับผลที่ได้จากการศึกษาโซเดียม-มอนต์โมริลโลไนต์ทางการค้า (SWy-2) จาก Source Clays Repository, Wyoming, USA

ได้ดัดแปรแร่มอนต์โมริลโลไนต์ในอนุภาคดินเหนียวที่แยกได้และ โซเดียม-มอนต์โมริลโลไนต์ทางการค้า โดยใช้เฮกซะเดซิลลามีน และศึกษาด้วยเทคนิค XRD, TGA และ FTIR แร่มอนต์โมริลโลไนต์ที่ดัดแปรแล้วนี้มีศักยภาพในการประยุกต์ทางเทคโนโลยีนาโนได้

สาขาวิชาเคมี ลายมือชื่อนักศึกษา__________
ปีการศึกษา 2547 ลายมือชื่ออาจารย์ที่ปรึกษา__________

NUTTINEE SUPAMATHANON : SEPARATION, CHARACTERIZATION AND MODIFICATION OF MONTMORILLONITE IN CLAY FROM NAKHONRATCHASIMA PROVINCE, THAILAND. THESIS ADVISOR : ASST. PROF. TRITAPORN CHOOSRI, Ph.D. 126 PP. ISBN 974-533-439-1

MONTMORILLONITE/VERTISOL SOIL/KAOLINITE/ILLITE/QUARTZ

Separation, characterization and modification of montmorillonite in clay from Nakhonratchasima Province were performed. The XRD and FTIR results confirmed that the dominant clay mineral in the separated fine clay was montmorillonite with minor to moderate amounts of kaolinite, illite, mixed illite-montmorillonite and traces amount of quartz ($\leq$ 2%). Twenty one soil samples were taken from vertisol soil which was known to have high content of montmorillonite in Muang District, Pimai District and Chokchai District. Sample pretreatments including removal of carbonates and organic matter were required prior to the separation and dispersion of clay from the soil. The particle size distribution analysis using the laser diffraction technique was carried out after Fe_2O_3 removal. All samples contained about 28.51-73.63% of the clay fraction. The fine clay particles (< 0.2 μm) which contained higher percentages of montmorillonite were fractionated by the process of centrifugation. The separated fine clay in the form of sodium-saturated was characterized with X-ray diffraction spectrometry (XRD) for the basal d-spacing; X-ray fluorescence spectrometry (XRF) for the chemical composition; scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for the morphology studies; Fourier transform infrared spectroscopy (FTIR) for the structural information; thermal analysis by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) to study the thermal properties. The results were comparable with those obtained from Na-montmorillonite (SWy-2), the commercial clay from Source Clays Repository, Wyoming, USA.

The separated fine clay and SWy-2 clay were modified using hexadecylamine and characterized with XRD, TGA and FTIR. The modified montmorillonite has potential for applications in nanotechnology.

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Nuttinee Supamathanon

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LIST OF ABBREVIATIONS

Å	Angstrom
et al	et alia (and other)
^oC	degree celcius
C.E.C.	cation exchange capacity
cm	centimeter
cps	counts per second
cpm	counts per minute
DTA	Differential thermal analysis
e.g.	for example
etc.	etcetera (and so forth)
FTIR	Fourier transform infrared
g	gram
h	hour
i.e.	id est (that is)
km^2	square kilometer
kV	kilovolt
m	meter
mA	milliampere
ml	milliliter
mg	milligram
mm	milimeter

LIST OF ABBREVIATIONS (Continued)

nm	nanometer
µm	micrometer
cm^{-1}	wavenumber
rpm	round per minute
SEM	Scanning electron microscope
%T	percent transmittance
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
USDA	United States Department of Agriculture
WDXRF	Wavelength dispersive X-ray fluorescence
XRD	X-ray diffraction
XRF	X-ray fluorescence

CHAPTER I

INTRODUCTION

Montmorillonite is a group of clay minerals, usually found in clay. Clay is a general term for inorganic material which is smaller than 2 µm in size, whereas clay mineral refers to a specific mineral which mainly occurs in the clay-sized fraction of soil (Moore and Reynolds, 1989). Most clay in natural setting has a phyllosilicate or sheet structure. Montmorillonite is also phyllosilicates with layer structure that contains large percentage of water trapped between the silicate sheets. The water content is variable. When water is absorbed by the clay structure, the clay tend to swell to several times of their original volume. Cation and organic compounds can be inserted or removed from the layer structures. This property makes montmorillonite a useful mineral, for example, it can be used as a starting material in several syntheses of the polymer-layered silicate nanocomposites, as a catalyst, as an absorbent, and many of the others (Velde, 1992 and Grim, 1962). Attempt had been made in this work to separate montmorillonite from clay.

After separation, montmorillonite was characterized physically and chemically and compared with the commercial montmorillonite by X-ray diffraction spectrometry (XRD), X-ray fluorescence spectrometry (XRF), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). In addition, thermal properties of montmorillonite were investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

Furthermore, since modified montmorillonite is now becoming the current interest as a new material with applications in the field of high technology, modification of the separated montmorillonite was pursued. The modified montmorillonite was prepared with alkyl-ammonium ion and characterized by the XRD, FTIR and TGA techniques.

1.1 Background of the problem and significance of the study

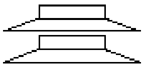
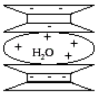
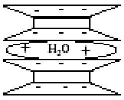
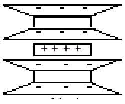
Phyllosilicate minerals are aluminosilicates with a layer structure, sometimes called layer silicates, consisting of planar layers of aluminum octahedral sheets and silicon tetrahedral sheets. These octahedral and tetrahedral sheets can be sandwiched together to form layers, and stacked on top of one another to form the different clay minerals.

Phyllosilicate minerals can be divided into 4 groups based on the number of sheets of silicon tetrahedra and aluminum octahedra in layer structure. Kaolinite, the so called 1:1 layer silicates has one silicon sheet and one aluminum sheet. Smectite which has two silicon sheets for every aluminum sheet is called a 2:1 layer silicates. Vermiculite is also a 2:1 layer silicates but has different properties from those of smectite. Chlorite which has two silicon sheets, one aluminum sheet plus a sheet of magnesium atoms between adjacent silicon sheets, is called a 2:1:1 layer silicates (Singer and Munns, 1999).

The most important property of clay minerals is the capacity of certain clay to change volume by absorbing water molecules or other polar ions into its structures.

This property is called the swelling or expanding. Thus, clay minerals can also be classified as swelling (expanding) and non-swelling (non-expanding) type (Table 1.1) (Velde, 1992).

Table 1.1 Summary of clay minerals properties.

Mineral	**Type**	**Ranges of CEC[*]** **[cmol/kg]**	**Structure**	**Shrink or Swell**
Kaolinite	1:1	2-10		No
Smectite	2:1	80-120		Yes
Vermiculite	2:1	100-180		Limited
Chlorite	2:1:1	15-40		No

CEC[*]: Cation exchange capacity

Montmorillonite is used in the manufacture of various catalysts and catalyst carriers in zeolites synthesis. Acid-treated and cation exchanged montmorillonites possess the ability to catalyze organic reactions. During the thirties and forties, acid-treated montmorillonites were the major catalysts in petroleum processing, though they were later replaced by zeolites which were more thermostable. The modified montmorillonites are versatile heterogeneous catalysts for a wide variety of organic reactions (Varma, 2002). The range of reactions that have been successfully performed using clay catalysts include addition, elimination, addition-elimination, substitution rearrangement, Diels-Alder reactions, oxidation-reduction and others (Nagendrappa, 2002).

Montmorillonite clays are used as additives in latex for the purposes of thickening and stabilizing (Anon, 1937). It is also used as emulsion stabilizers, for example, in rubber-base paints, and in rubber adhesives (Grim, 1962).

In soap, highly colloidal sodium montmorillonite clays improve detergent action of soap and may be used as builders. Sodium montmorillonites have water-softening action by exchangeably replacing calcium and magnesium with sodium. During washing, the clay helps to keep the dirt in suspension. Like soap, such clay emulsifies oil and grease. The properties of montmorillonite mentioned above have led to the suggested use of clays in a variety of cleaning and polishing compounds (Grim, 1962).

Montmorillonites are employed satisfactory for animal bedding, as an absorbent and deodorizing agent and as pelleted animal food of all kinds (Grim, 1962).

One application of montmorillonite is as a binder for foundry moulding sands and in the pelletizing of iron ores. Because of its good bonding characteristics, montmorillonite is also used to provide a bond in brake linings and a plasticiser in refractory, abrasive and ceramic mixes (Christie, Thompson and Brathwaite, 2000).

Montmorillonite is a very effective agent for beverage clarification for such wine, cider. Saywell (1935) pointed out that the colloidal impurities in wine carried positive charges and that could be coagulated and removed by stirring a small amount of a negatively charged material into the wine. The montmorillonite particles attracted the wine impurities and settled out together. In addition, it has been indicated that montmorillonite adsorbed and removed about 50% of the iron in the original wine (Saywell, 1935).

Montmorillonites have been successfully used in the synthesis of polymer-clay nanocomposites. Nanocomposites are new class of composites. The term nanocomposite describes a two-phase material where one of the phases is dispersed in the second one on a nanometer level. Polymer-clay nanocomposites have many advantages, compared to the traditional reinforcing agents for plastic. Polymer-clay nanocomposites provide better performance properties in modulus and tensile strength, increase barrier properties and increase dimensional stability. They also provide the improvement of heat distortion temperature, dyeing property and flame retardation property (Kornmann, 1999; Alexandre and Dubois, 2000; LeBaron, Wang and Pinnavaia, 1999).

The organic clay which is the montmorillonite modified with organic compounds such as amines, ammonium chloride, silanes and others, also has tremendous applications as well. They have been used in nondripping paints, greases, printing inks, drilling muds and cosmetics (Christie, Thompson and Brathwaite, 2000). Besides, modified montmorillonite with as low as 4 wt% is used as filler in the synthesis of polymer-clay nanocomposites that show dramatic improvement of mechanical properties and barrier properties (Okada et al., 1990).

Other application of modified montmorillonite is to make Pillared Clay (PILC), which is two-dimensional layer materials developed in the late 1970s as a catalyst for crude oil cracking processes. This material is typically prepared by replacement of the interlayer exchangeable cations in smectite clay by metal complex cations which are converted by calcination into oxide pillars between the clay layers. Various kinds of metal-PILCs have been introduced such as Al-PILCs, Zr-PILCs, Cr-PILCs, Si-PILCs, Fe-PILCs and Ti-PILCs. It has been found that the cation surfactant-treated PILCs with montmorillonite as a starting material, show an interesting affinity and capacity in removal of phenolic compounds. These results suggest a waste water treatment application of this modified montmorillonite (Wibulswas, White and Rautiu, 1999). They have been used to prepare catalysts for large or small scale organic syntheses (Adams, 1987).

As mentioned above, clay minerals are found in nature and distributed in almost every continent. It has been extracted from soil as a primary raw material. Montmorillonite is a clay mineral concentrated in vertisol soil, about 3360 km^2, can be found in Thailand. There are approximately 169 km^2 of vertisol soil in Nakhonratchasima Province (Panichapong, 1982; Vijarnsorn, 1982). Both montmorillonie and modified montmorillonite are used in large diversity of industrial processes. They are also the starting materials in several syntheses of zeolite, classical oxide ceramics, mesoporous materials and others. Accordingly, separation of montmorillonite from clay is the main interest for this work. Moreover, since the commercial montmorillonite is very expensive (about 50 U$ per kilogram) and the price is increasing for modified montmorillonite, value added of the natural clay minerals is also the reason that motivates this research. At present commercial grade montmorillonites which have limited applications are available from some manufacturers.

In this work, attempts were made to separate and characterize montmorillonite in clay from Nakhonratchasima vertisol soil. After that the montmorillonite were modified with alkylammonium ion and characterized. The results were compared with the commercial ones.

1.2 Research objectives

1.2.1. To separate montmorillonite in clay from Nakhonratchasima Province.

1.2.2. To characterize montmorillonite obtained from the separation and compare the results with the commercial montmorillonite.

1.2.3. To modify the separated montmorillonite and the commercial montmorillonite with alkylammonium ion.

1.2.4. To characterize the two modified montmorillonites.

1.3 Scope and limitation of the study

The studies were conducted on montmorillonite in vertisol soil from Nakhonratchasima Province and the commercial montmorillonite from the Source Clays Repository, Crook County, Wyoming, USA.

CHAPTER II

LITERATURE REVIEWS

2.1 General overview of montmorillonite

Damour and Salvetat proposed the name Montmorillonite in 1847 after the name Montmorillon in France (Damour and Salvetat, 1847). In older literatures, montmorillonite was a synonym for this mineral group, but today montmorillonite is considered as a specific smectite mineral (Olson, Thompson and Wilson, 2000).

Montmorillonite is an aluminosilicate with a layer structure, classified as phyllosilicate. The layer structure is composed of one aluminum octahedral layer sandwiched between two silicon tetrahedral layers. The tetrahedral sheet is composed of silicon-oxygen tetrahedra linked to neighboring tetrahedra by sharing three corners to form a hexagonal network (Figure 2.1). The fourth corner of each tetrahedron (the apical oxygen) points into and forms a part of the adjacent octahedral sheet. The octahedral sheet is usually composed of aluminium or magnesium in six-fold coordination with oxygen from the tetrahedral sheet and with the hydroxyl group. Individual octahedra are linked laterally by sharing edges (Figure 2.2). Tetrahedral and octahedral sheets taken together form a layer, which may join to each other in a clay crystallite by interlayer cations, using van der Waals and electrostatic forces, or hydrogen bondings (Spark, 1995; Grim, 1953; Newman, 1987; Batter, 1981; White, 1997). Figure 2.3 shows a structure of montmorillonite as proposed by Grim (1962) (U.S. Geological Survey, www, 2001).

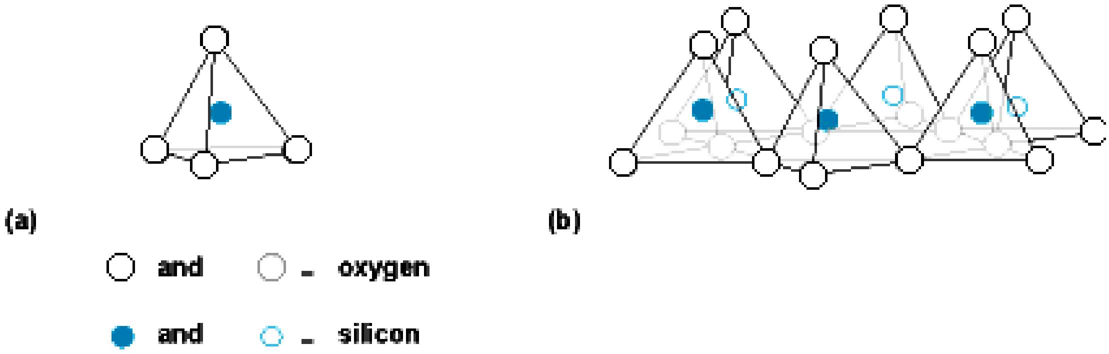


Figure 2.1 Diagrammatic sketch showing (a) single silica tetrahedron and (b) sheet structure of silica tetrahedrons arranged in a hexagonal network (Grim, 1953).

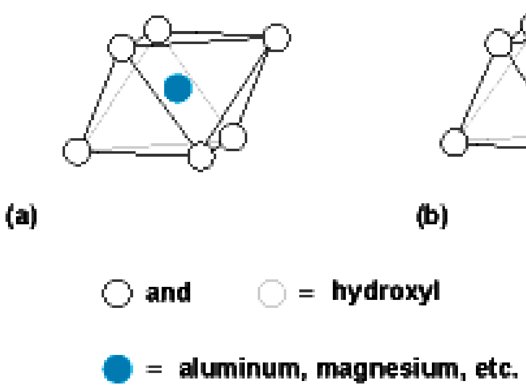


Figure 2.2 Diagrammatic sketch showing (a) single octahedral unit and (b) sheet structure of octahedral units (Grim, 1953).

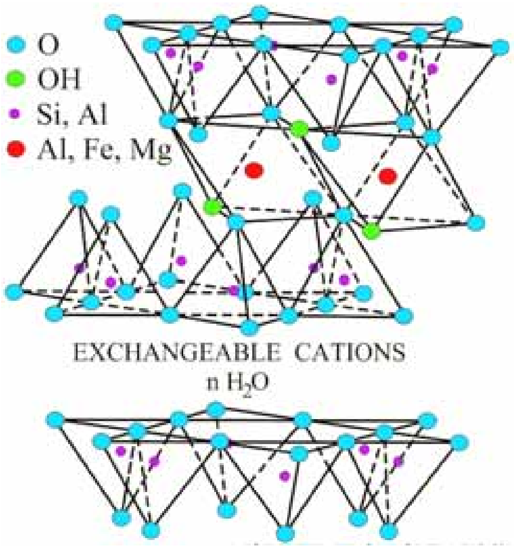


Figure 2.3 Structure of montmorillonite.

Ideal formula for montmorillonite is $(M^{+}{}_{x})^{ex}\ [(Si_8)^{tet}\ (M(III)_{4-x}\ M(II)_x)^{oct}\ O_{20}\ (OH)_4]^{x-}$ where M^{+} is the exchangeable cation (e.g. Na^{+}) present in the interlayer, M(III) and M(II) are non-exchangeable octahedrally coordinated trivalent and divalent cations (e.g. Al^{3+} and Mg^{2+}) respectively, and x, the layer charge, has the values between 0.5 and 1.2 (Varma, 2002).

Isomorphous substitution, which occurs when the mineral forms, is the substitution of one atom by another atom of similar size in the crystal lattice without disrupting the crystal structure of the mineral (Glossary of Soil Science Terms, 1987). The size of the cationic radius determines which cations can substitute in the silica and octahedral sheets. In tetrahedral sheet, Si^{4+} is usually substituted by Al^{3+}. In octahedral sheets, the dominate cation is Al^{3+} but Mg^{2+}, Fe^{3+}, Fe^{2+} and Zn^{2+} may substitute for Al^{3+} (see Figure 2.3). These isomorphous substitutions lead to the net negative charges on the clay structure which must be satisfied by the presence of charge balancing cations, such as Ca^{2+} and Na^{+}, somewhere else in the structure. The interlayer is hydrated which allows cations to move freely in and out of the structure. Because the interlayer is open and hydrated, cations may be present within the interlayer to balance negative charges on the sheet themselves. These cations between the layers are part of the cation exchange capacity (CEC) of the soil (University of Minnesota, WWW, 2003; Miller and Gondiner, 2001).

The properties of montmorillonite are summarized in Table 2.1

Table 2.1 Summaries of montmorillonite properties (Soil and Water Science, University of Florida, www, 2004).

Mineral	**Type**	**Interlayer condition / Bonding**	**CEC [cmol/kg]**	**Swelling potential**	**Specific surface area [m^2/g]**	**Basal spacing [Å]**
Montmorillonite	2 : 1 (expanding)	great expansion, very weak bonding	80 - 150	high	700 - 800	9.8-18 +

Montmorillonites show very weak to weak bonding due to various cations between the sheets, therefore, they exhibit a great ability to expand, especially under wet condition. The smaller the size of a fragment, the greater the ratio of its surface to volume, which defines the specific surface area. The high cation exchange capacity of soil with high amount of 2:1 type clay originates mainly from the isomorphous substitutions. These negatively charged sites are not affected by pH and constituted the permanent charges. Montmorillonite has a relatively large amount of isomorphous replacements resulting in a large number of exchange sites and a high CEC (Soil and Water Science, University of Florida, www, 2004). The distance from the center of one montmorillonite layer to the center of the next, ranges from 9.6 Å when all the water is removed to 21.4 Å or more when much water is present. Still, there is enough attraction to hold the layers together in particles several layers thick (Troch and Thompson, 1993).

2.2 Montmorillonite in soil

Smectite is often dominant in soils formed under alkaline weathering conditions. Thus, smectite is commonly the major clay mineral in vertisols formed from diverse parent materials in different areas of the world.

Vertisols are clay soils which exhibit impressive volume change due to shrink/swell processes when soil moisture condition changes. Vertisols have a high content (>30%) of sticky, swelling and shrinking type clays to a depth of 1 m or more (Buol, Hole and McCracken, 1989; Brady and Weil, 2000).

Thai Vertisols occupy about 3360 km^2 throughout the country. They are developed from transported materials mostly originating from limestone, marl, basalt and andesite. A dark color, wide and deep cracks in the dry season and high smectite content are the most common properties of the Thai vertisols (Vijarnsorn, 1982). The most notable vertisols formation in Thailand is in Lopburi Province which amounts to 1540 km^2. There is over 169 km^2 of vertisols in Nakhonratchasima Province (Panichapong, 1982; Vijarnsorn, 1982).

2.3 Soil fractionation for mineralogical analyses

Separation of the soil into the major size fractions is a prerequisite for mineralogical analyses. It will provide a rough sorting between phyllosilicates present mostly in the fine fractions and other silicates present mainly in the coarser fractions. These minerals have distinct requirements for their analyses and identification.

During 1846-1916, the Swedish soil scientist, Albert Mauritz Atterberg, studied the plasticity of soil. The investigation of the flocculation of different soil fractions obtained by sedimentation had been made. The Atterberg sedimentation technique is still an important method for the separation of clays and clay minerals into fractions. Atterberg recommended the following notation: clay < 0.002 mm (in diameter), sand 0.02-2 mm and gravel > 2 mm (Atterberg, 1905; 1910).

There are many ways to concentrate minerals in soils in order to facilitate their characterization. The most commonly employed pretreatment techniques used are the followings: carbonates removal, organic matter removal, iron oxide removal and size fractionation (Genrich and Bremner, 1974; Kunze and Dixon, 1986; Doesburg, 1996; Buhrke, Jenkins and Smith, 1998).

Canadian Society of Soil Science has proposed 4 methods that can be used for the separation of minerals: (1) water dispersion, (2) dispersion in water and sonification, (3) dispersion in water at pH 9 after removal of organic matter, and (4) dispersion in water after organic matter and iron oxide removals. The pretreatment severity increases from the first method to the fourth. The method used should be selected according to the objectives of the study (Kimpe, 1993).

Mineral particles occur in various size ranges. The USDA system of size classification is shown in Table 2.2. It is often necessary to fractionate soil and clay samples to one of these size ranges to elucidate and quantify specific mineral species present. Coarse size fractions are obtained either by wet or dry sieving through a standard set of sieves. The fine fractions, starting from very fine sand, are separated by a combination of wet sieving and gravity or centrifugal sedimentation (Buhrke, Jenkins and Smith, 1998).

Table 2.2 USDA system of size classification.

Mineral	**Size (mm)**
Very coarse sand	2.00-1.00
Coarse sand	1.00-0.50
Medium sand	0.50-0.25
Fine sand	0.25-0.10
Very fine sand	0.10-0.05
Coarse silt	0.05-0.005
Fine silt	0.005-0.002
Clay	<0.002

Montmorillonite occurs as small aggregates of irregular shape. The size is usually smaller than 0.5 μm but depended on the type of cations. Na-saturated size is very fine gel where as Ca-saturated occurs as coarser flake shaped particles. Since smectite minerals are more resistant to chemical weathering, they tend to persist in greater quantities in the finer clay fractions. So attempts were made to separate the fine clay (0.2 μm) fraction. The size distribution of various soil minerals are shown in Figure 2.4.

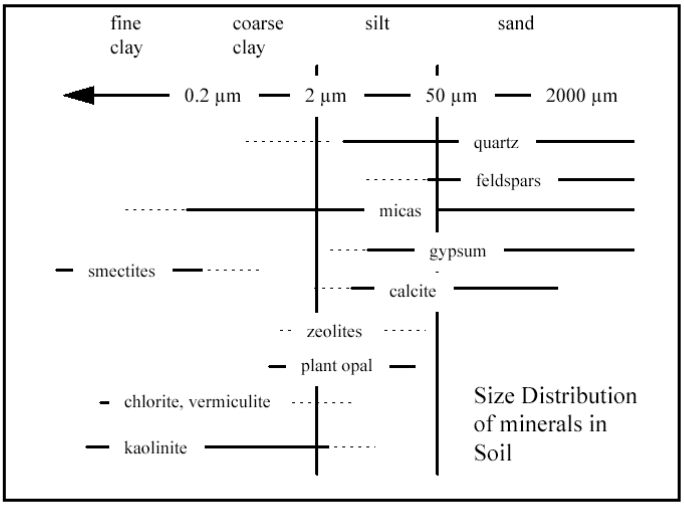


Figure 2.4 Size distribution of minerals in soil (College of Engineering, University of Saskatchewan, www, 2005).

In separation of particle size fractions, soil clay samples are normally separated into two or more subfractions before X-ray diffraction analysis. The customary subfractions are coarse (2-0.2 µm), medium (0.2-0.08 µm) and fine clay (< 0.08 µm). Separation of particles into two subfractions (2-0.2 µm and < 0.2 µm) is generally sufficient for most purposes.

The suspension or centrifuge method is then used to separate other fine (clay and silt) fractions either by gravity sedimentation or centrifugation. The settling times required to separate various size ranges, based on Stoke’s law were presented in extensive nomographs and tables by Jackson (Jackson, 1979).

An integrated form of Stoke’s law, as proposed by Svedberg and Nichols (1923), allows calculation of the time requires for sedimentation of particles of particular diameter and specific gravity under centrifugal acceleration. The formula takes the following form for separation of particles in a tube centrifuge:

$$t = \frac{n \log R/S}{3.81N^2 r^2 \Delta s}$$

Where t is the time in seconds, R is the radius in centimeters of rotation of the top of the sediment in the tube, S is the radius in centimeters of rotation of the surface of the suspension in the tube (see Figure 3.9), *n* is the viscosity of liquid in poises at the existing temperature, N is the revolutions per second, r is the particle radius in centimeters, and Δs is the difference in specific gravity between the particles and the suspension liquid (Whitting and Allardice, 1986). For the convenient units of the time in minute, t_{min}, N_m as rpm, and particle diameter in microns, D_μ, the following equation holds:

$$t_{min} = \frac{63.0 \times 10^8 \, n \log R/S}{N_m^2 \, D_\mu^2 \, \Delta s}$$

In this work, carbonates removal and organic matter removal were selected for soil pretreatment before using water dispersion to separate clay minerals. Separation of fine clay fraction (0.2 μm) by centrifugation were performed. In this procedure, sonification was not necessary, as all aggregates had been decomposed, leaving only individual mineral particles. Also, water dispersion would be less time consuming than any other separation procedures.

2.4 Characterization techniques

Several techniques can be utilized for the characterization of the clay minerals. In this work XRD, XRF, FTIR, SEM, TEM and thermal analysis were used in the identification of clay minerals.

2.4.1 X-ray diffraction spectrometry

XRD technique is the most important method in the primary investigative for identifying the variety of crystalline mineral species present in the clay fraction of soils (Brown, 1961; Brindley and Brown, 1980; Dixon and Weed, 1989; Wilson, 1987 and Bergaya et al., 2005). In XRD method, X-rays are diffracted by the atomic layers in the crystals. In mineralogical studies, the diffracted X-rays are used to measure the dimensions of the atomic layers in the crystals. Since each different mineral has a distinct set of atomic layers spacings (called d-spacings), the suite of measurements can be used to identify the mineral. All crystalline minerals in the sample can be identified from one XRD scan, if they are present in sufficient abundance (Lewis and McConchie, 1994). The relationship between the wavelength of the X-rays used, the angle between the incident and the diffracted X-rays, and the distance between the atomic layers causing the diffraction is given by the Bragg's law equation:

$$n\lambda = 2d\sin\theta$$

where the integer n is the order of the diffracted beam which can be any whole number, λ is the wavelength of the incident X-rays beam, d is the distance between adjacent planes of atoms (the d-spacings), and θ is the angle of incidence of the X-rays beam. Known values of λ and θ, can be used to calculate the d-spacings. The geometry of an XRD unit is designed to accommodate this measurement (Figure 2.5). The characteristic set of d-spacings generated in a typical X-rays scan provides a unique "fingerprint" of the mineral or minerals present in the sample. When properly interpreted, by comparison with standard reference patterns and measurements, this "fingerprint" allows for the identification of the material.

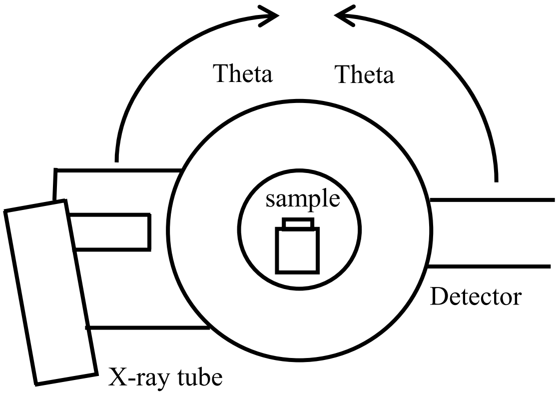


Figure 2.5 Simplified sketch of one possible configuration of the X-rays source (X-rays tube), the X-rays detector, and the sample during the X-rays scan. In this configuration, the X-rays tube and the detector both move through the angle theta (θ) while the sample remains stationary.

If the instrumentation is available, XRD is the most efficient and effective method to identify clay minerals that are present in soil. In principle, no two minerals have exactly the same distances between planes of atoms; therefore, diffraction angles and patterns are distinctive for individual minerals. XRD is a powerful tool for the identification of soil minerals in all size fractions. Because the interplanar spacings of some phyllosilicate minerals are variable and depend on the saturation cation and the presence of water or other polar molecules, thoroughly tested protocols have been developed to assist in the XRD characterization of clay minerals (Whitting and Allardice, 1986). From the standpoint of XRD analyses, phyllosilicates differ from one another primarily in the z-dimension. Unlike most other minerals, phyllosilicates are often identified by X-ray analyses of samples that are oriented to emphasize those differences. Well-oriented samples can be produced by sedimenting a suspension of clay onto a porous ceramic tile or onto a glass microscope slide. A number of the other techniques have been developed for the same purpose (Moore and Reynolds, 1997). In addition, d-spacings that are perpendicular to the basal plane of atoms change in response to saturation with different cations, intercalation with organic compounds, and heating. By using consistent and well-planned pretreatment of the sample, the investigator can readily identify phyllosilicate minerals from the sample XRD pattern. In the discussion that follows, emphasis is placed on the differentiation of phyllosilicates by analyzing d(001) spacings of oriented samples (See Appendix B).

2.4.2 X-ray fluorescence spectrometry

XRF can be used to obtain an excellent chemical analysis of a very small quantity of clay minerals. XRF has the advantages of being non-destructive, multi-elemental, fast and cost-effective analytical method. Furthermore, it provides a fairly uniform detection limit across a large portion of the periodic table and is applicable to a wide range of concentrations, from a 100% to a few parts per million.

The X-ray fluorescence principle is depicted in Figure 2.6. An inner shell electron is excited and ejected by an incident photon in the X-ray region. During the de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks lead to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the relevant or absolute elemental concentration (semi-quantitative or quantitative analysis). A typical XRF spectrometer arrangement (Figure 2.6) includes a source of primary radiation (usually a radioisotope or an X-ray tube) and an equipment for detecting the secondary X-rays. (University of Ioannina, www, 2002).

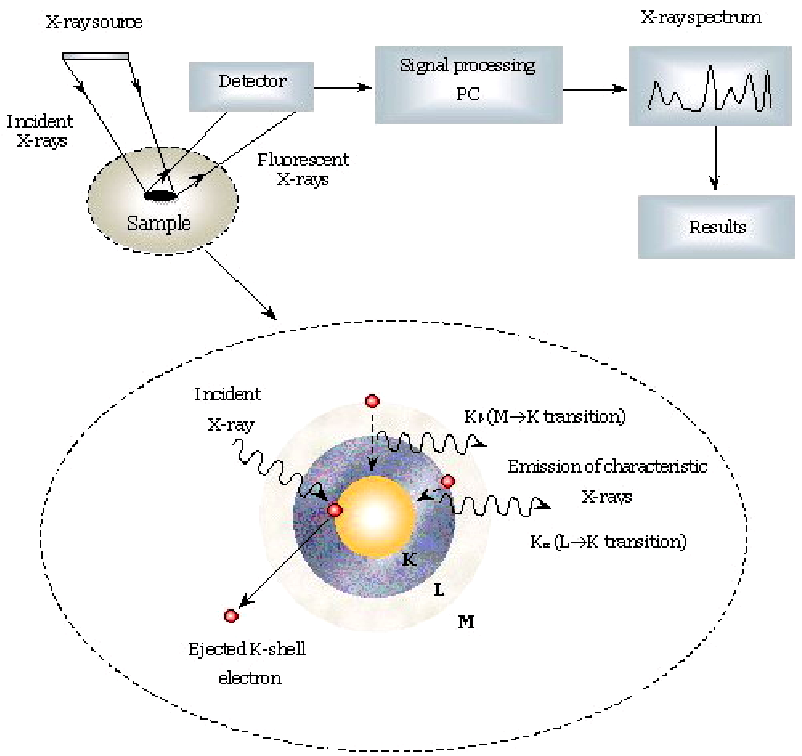


Figure 2.6 The principle of XRF and the typical XRF detection arrangement (University of Ioannina, www, 2002).

2.4.3 Fourier transform infrared spectroscopy

FTIR is used to distinguish between different types of clay minerals and to derive information concerning their structures, compositions and structural changes upon chemical modification (Russell, 1987; Velde, 1992; Russell and Fraser 1994; Madejov′a, 2003).

The absorption of infrared radiation by clay minerals depends critically on atomic masses, lengths, strengths and force constants of interatomic bonds in the structures of these minerals (Russell, 1987). Infrared radiation is used to probe the energy levels of molecules. The total energy of a molecule can be thought of as a combination of transitional, vibrational, rotational, and electronic energies. These types of molecular energies are quantized, and only discrete energy levels are permitted. Therefore, molecules absorb energy inputs only at those nonarbitrary levels. Infrared energy corresponds to rotational and vibrational transitions of molecules. Since molecules in solid rarely rotate freely, IR studies of minerals are primarily concerned with vibrational transitions (Olson, Thompson and Wilson, 2000).

IR absorption occurs only at certain wavelengths, which depend on the precise nature of the molecular bonds present in the sample. Therefore, infrared spectroscopy provides a means of determining which functional groups are present in a sample. Furthermore, infrared spectra are also quantitative: the absorbance is directly proportional to the concentration of absorbing species (Lewis and McConchie, 1994).

2.4.4 Scanning electron microscope

Scanning electron microscope is used to determine the morphology of clay minerals. SEM enables the investigator to appreciate fully the heterogeneity of clay minerals, to visualize the various mineral components in their distinct growth forms, and how they are related in terms of overall microfabric and texture. The flux of secondary and backscattered electrons from material to form an intensity image of the material bombarded by the electron beam are the basis of SEM. The resulting cathode tube realization indicates the three-dimensional aspect of the sample. This is very useful in the identification of textures and shapes of mineral grain aggregates. The definition or resolution of the image is in the order of 0.01 μm. (Velde, 1992; White and Dixon,1995). Scanning electron microscope reveals detailed information on the morphology, distribution and phase relationships of diagenetic minerals and on the shape and distribution of pore systems.

A schematic presentation of the scanning electron microscope is shown in Figure 2.7. The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons. The stream is condensed by the first condenser lens, used to form the beam and limit the amount of current in the beam. This lens works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam. The second condenser lens forms the electrons into a thin, tight, coherent beam. A user selectable objective aperture further eliminates high-angle electrons from the beam. A set of coils then "scans" or "sweeps" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed. The objective lens focuses the scanning beam onto the part of the specimen desired. When the beam strikes the sample (and dwells for a few microseconds), interactions occur inside the sample and are detected with various instruments. Before the beam moves to its next dwell point, these instruments count the number of interactions and display a pixel on a cathode ray tube whose intensity is determined by this number (the more reactions the brighter the pixel).

Figure 2.8 shows the SEM image of Na-montmorillonite, in which the individual particles are difficult to notice, the general appearance being that of a fluffy, irregular mass of agglomerated particles.

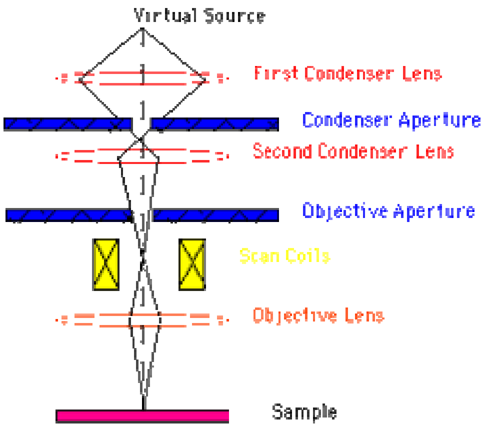


Figure 2.7 Schematic presentation of a scanning electron microscope (Center for Materials Research and Analysis, University of Nebraska-Lincoln, www, 2005).

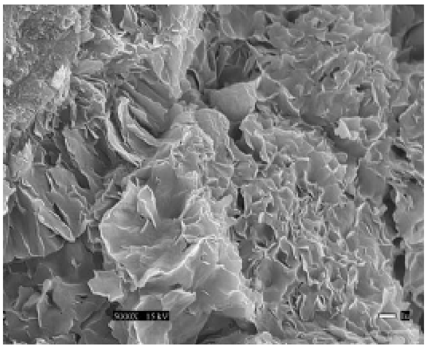


Figure 2.8 Scanning electron micrograph of Na-montmorillonite texture (Allo and. Murray, 2004).

2.4.5 Transmission electron microscope

TEM is an extremely versatile and powerful technique for examining clay minerals either in the dispersed or the bulk state. A major advantage is that the instrument can provide direct morphological, structural and chemical information on selected clay particles if a microprobe analyzer is fitted (Nadeau and Tait, 1987; Velde, 1992).

In transmission electron microscope, a beam of highly focused electrons is directed toward a thin sample (<200 nm). These highly energetic incident electrons interact with the atoms in the sample producing characteristic radiation and particles, providing information for material characterization. Information is obtained from both deflected and non-deflected transmitted electrons, backscattered and secondary electrons, and emitted photons.

A schematic presentation of the transmission electron microscope is shown in Figure 2.9. The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons. This stream is focused to a small, thin, coherent beam by condenser lenses 1 and 2. The beam is restricted by the condenser aperture, knocking out high angle electrons. The beam then strikes the specimen and parts of it are transmitted. This transmitted portion is focused by the objective lens into an image. The objective aperture enhancing contrast by blocking out high-angle diffracted electrons and the selected area aperture enabling the examining of the periodic diffraction of electrons by ordered arrangements of atoms in the sample. The image is passed down the column through the intermediate and projector lenses, being enlarged all the way. The image strikes the phosphor image screen and light is generated. The darker areas of the image represent those areas of the sample that fewer electrons were transmitted through (they are thicker or denser). The lighter areas of the image represent those areas of the sample that more electrons were transmitted through (they are thinner or less dense).

Mineral in smectite group is quite varied morphologically, although most specimens are characterized by extremely fine-grained, poorly defined particles, with diffused outlines and curled edges. Figure 2.10 shows TEM image of montmorillonite. Montmorillonite particles can therefore be regarded as aggregates, and indeed, a foliated, lamellar aggregate structure is often obvious (Nadeau and Tait, 1987).

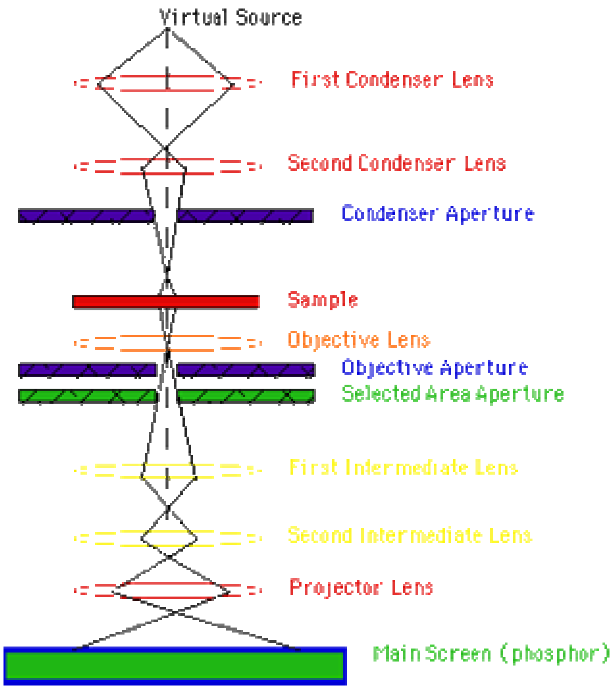


Figure 2.9 Schematic presentation of a transmission electron microscope (Center for Materials Research and Analysis, University of Nebraska-Lincoln, www, 2005).

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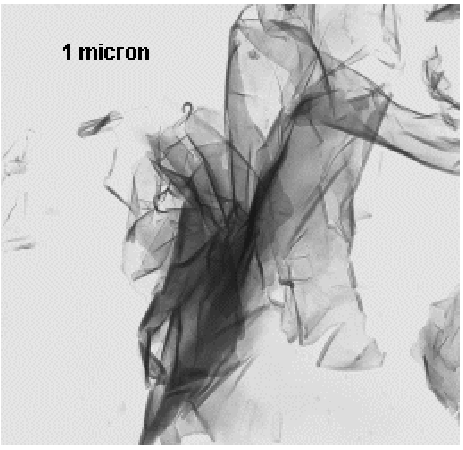


Figure 2.10 Transmission electron micrograph showing morphology of montmorillonite (Industrial Material Institute, National Research Council Canada, www, 2003).

2.4.6 Thermal analysis

Thermal analysis comprises a group of techniques in which the changes in mass, temperature, or enthalpy of material are measured as the temperature is varied in a controlled way. In the studies of layer silicates, thermal analysis is used for the identification and quantification of the minerals, as well as for determining of the thermodynamic and kinetic parameters of reactions involved the minerals. Thermal analysis techniques that are commonly applied to the studies of layer silicates are thermogravimetric analysis and differential thermal analysis (Grim, 1953; Paterson and Swaffield, 1987; Worrall, 1986; Velde, 1992; Olson, Thompson and Wilson, 2000).

2.4.6.1 Thermogravimetric analysis

TGA is a technique for determining the weight loss of a sample as it is being heated at a controlled rate . The weight changes are recorded as a function of temperature, i.e., a thermogravimetric curve, and provide quantitative information about the substance under investigation.

2.4.6.2 Differential thermal analysis

In DTA, the temperature difference between a sample and a thermally inert reference material is measured as they are heated together at a controlled rate. The measurement is therefore the energy changes as heat is either taken up or released by the sample. Endothermic reactions in the sample are indicated when the sample temperature is less than that of the reference material. If the difference in temperature between the sample and the reference is positive, an exothermic reaction has occurred. Application of differential thermal analysis depends on two conditions: (1) that chemical or phase-change reactions (including dehydration) in the sample involve a heat change either in entropy, enthalpy, or both. These heat changes can be either endothermic (heat consuming) or exothermic (heat releasing) and (2) that these changes occur over a limited temperature range. In DTA studies, two parameters are recorded: the temperature at which the reaction occurs, and the heat change involved.

Figure 2.11 shows TGA and DTA curves of bentonite, a natural clay containing the mineral montmorillonite. The differential thermal curves present endothermic peaks characteristic of adsorbed water at 146^{o}C and present undulations at approximately 220^{o}C, due to the presence of water coordinated to calcium and magnesium. This confirms the nature of polycationic clays. A second endotherm corresponds to the dehydroxylation reaction at 580^{o}C. The sample also presents an endothermic band between 500^{o}C and 650^{o}C, characteristic of the hydroxyl loss of bentonite rich in iron. Also the curve presents endo-exothermic peaks characteristic at

865°C and 930°C from formation of α or β-quartz of mullite. The thermogravimetric curve presents a slope related to the loss of hygroscopic water at temperature around 100-350°C and the loss of hydroxyl groups at temperature around 350-650°C (Amorim et al., 2004).

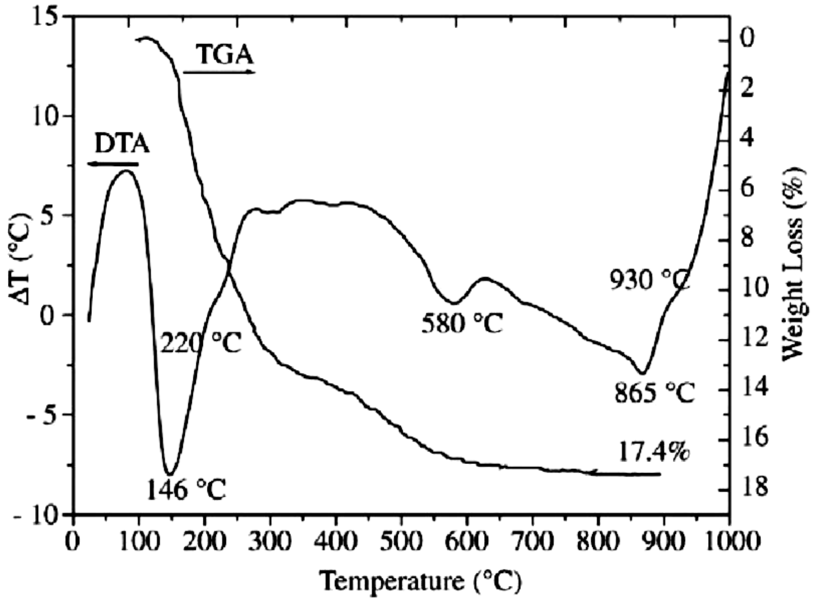


Figure 2.11 TGA and DTA curves of bentonite (Amorim et al., 2004).

2.5 Laser diffraction method

Laser diffraction method was introduced for the determination of particle size distribution (PSD). This method had been used in sedimentology and soil science for more than a decade due to its overwhelming advantages, eliminating the major limitations of the classical methods (hydrometer and pipette) and providing data in more detailed and digital formats (Singer et al., 1988; McCave and Syvitski, 1991). The principle of this method is that particles of a given size diffract light through a given angle. The angle increases with decreasing in particle diameter. A parallel beam of monochromatic light passes through a suspension in a sample cell, and the diffracted light is focused onto a detector. The detectors measure the distribution of scattered light in term of density. A lens, placed between the illuminated samples with the detector at its focal point, focuses on the undiffracted light to a point at the center and leaves only the surrounding diffraction pattern, which does not vary with particle movement. A stream of particles can, therefore, be passed through the beam to generate a stable diffraction pattern. A microcomputer is connected with an optical bench and controls every function of the instrument. PSD is presented in volume units, and can also be expressed in surface area units or number of particles.

To calculate the particle sizes from light intensity sensed by detectors, two diffraction theories are adopted: Fraunhofer and Mie, the former being a limited case of the Lorentzi-Mie theory (Loizeau et al., 1994). Both theories assume that the particles are spherical in shape. In other words, the particle dimension calculated is the optical spherical diameter, which is the equivalent cross sectional diameter (Loizeau et al., 1994). Based on Fraunhofer theory, the relation between the angular distribution of light intensity I and particle radius r can be expressed as (Singer et al., 1988):

$$I(\theta) = \frac{1}{\theta^2} \int_0^\infty r^2 n(r) J_1^2(\theta k r)\,dr \quad \left\{ k = \frac{2\pi}{\lambda} \right\}$$

where θ is the scattering angle; $n(r)$ is the size distribution function; λ is the wavelength of the laser beam; and J_1 is the Bessel function of the first kind. Fraunhofer theory is inapplicable when particle diameter is close to the wavelength of light as the refraction of particles in this size range become considerable (Loizeau et al., 1994). When Mie theory, which is thought to better describe scattering mode of very fine particles, is adopted, the refractive index *R* of fluid and particles of a soil should be considered in the equation above. Figure 2.12 illustrates the main components and arrangement of laser diffraction by Malvern instruments.

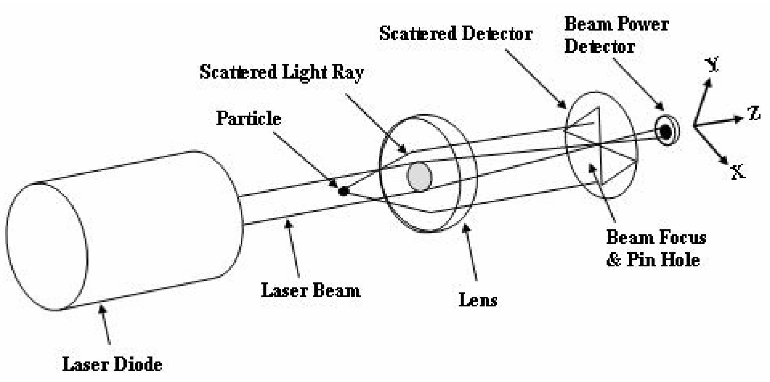


Figure 2.12 Schematic diagram showing the main components and arrangement of laser diffraction/Mie theory (Malvern instruments Ltd, www, 2005).

2.6 Modification of montmorillonite

Montmorillonites are often modified through an ion exchange process in which the interlayer cations are substituted by cationic surfactants such as alkylammonium ions. The intercalation of these small molecules between the layers reduces the forces that hold the stacks together and the resulting modified clays (or organoclays) are more compatible with the organic polymers. This property was first discovered by Jordan in 1949 and later by Weiss in 1963. Alkylammonium ions can be intercalated easily between the clay layers and offer a good alternative to amino acids for the synthesis of nanocomposites. The most widely used alkylammonium ions are based on primary alkylamines put in an acidic medium to protonate the amine function. Their basic formula is CH_3-$(CH_2)_n$-NH_3^+ where n is between 1 and 18. Alkylammonium ions based on secondary amines have also been successfully used (Wang and Pinnavaia, 1998).

The cation-exchange process of linear alkylammonium ions is described in Figure 2.13.

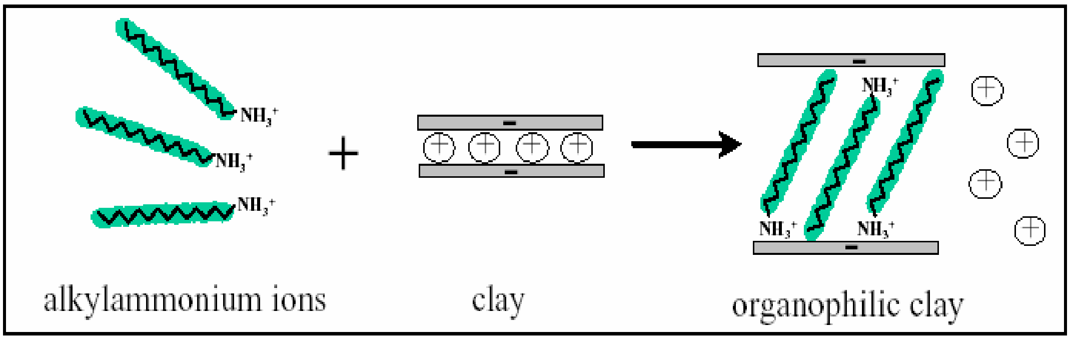


Figure 2.13 The cation-exchange process between alkylammonium ions and cations initially intercalated between the clay layers.

In Figure 2.13, the alkylammonium ions adopt a paraffin type structure (clay with high layer charge density) and the spacing between the clay layers increases by about 10 Å. The presence of alkylammonium ions permit to lower the surface energy of the clay so that organic species with different polarities can get intercalated between the clay layers.

The most important properties of the organic derivatives of montmorillonite with long alkyl chains, in particular with alkylammonium ions, are organophilicity, ability to swelling and the formation of thixotropic gel in organic media. Due to these properties, the organic derivatives of montmorillonite found a wide applications in industry as structure-forming and thickening agents in greases, paints, lacquers, plastisols, glues, drilling fluids, cosmetics, and other materials (Jordan, 1963; Nahin, 1963; van Olphen, 1977; Jones, 1983; Lagaly, 1986).

CHAPTER III

MATERIALS AND METHODS

3.1 Sampling sites

Sampling sites of vertisol soil which known to contain high percentages of montmorillonite were defined by using the soil map (scale 1:50,000) from the Detailed Reconnaissance Soil Map of Nakhonratchasima Province and by using the ThaiPedon 1.0 program provided by the Land Development Department, Ministry of Agriculture and Cooperatives, Bangkok (ThaiPedon 1.0 program, CD-ROM, 2001). Map of vertisol soil distribution in Nakhonratchasima Province is obtained from ThaiPedon 1.0 program, is shown in appendix A. Seven sampling sites were located in three districts with two sites in Muang District, three sites in Pimai District and two sites in Chokchai District. Global Position System (GPS) was being used to specify the exact location of the sampling points during the field sampling.

Area A: Muang District, 2 sampling points in Tambol Muenwai

1. Ban Tanlon, position; 48P 0184141, UTM 1661017
2. Ban Natom, position; 48P 0184495, UTM 1662098

Area B: Pimai District, 3 sampling points in Tambol Chiwan

1. Ban Nonphaniam, position; 48P 0236892, UTM 1698233
2. Ban Phaniam, position; 48P 0235262, UTM 1699311
3. Ban Nontako, position; 48P 0236854, UTM 1700115

Area C: Chokchai District, the first sampling point was in Tambol Chokchai and the second sampling point was in Tambol Tayiam

1. Ban Bungthapprang, Tambol Chokchai, position; 48P 0199885, UTM 1633476
2. Ban Donphlai, Tambol Tayiam, position; 48P 0199812, UTM 162515

The sampling sites were selected from the least disturbed areas. The soil samples were taken from three different depths for each site; 0-30 cm, 30-70 cm and 70-100 cm. Hand auger was used to gather about 2 kilograms each of the soil samples and put in the labeled plastic bag. The sample were kept in the refrigerator for later analyses.

3.2 Sample nomenclature

The soil samples were named using letter and digit as follows:

The first letter: represented the sampling sites which were;

A: Muang District

B: Pimai District

C: Chokchai District

The first digit: represented the location of sampling point in each district which were from1 to 3.

The second digit: represented the depth range where the samples were taken;

1: depth range of 0-30 cm.

2: depth range of 30-70 cm.

3: depth range of 70-100 cm.

Example:

A1-1 Soil sample taken from Muang District at sampling point 1 from the depth range of 0-30 cm.

A2-2 Soil sample taken from Muang District at sampling point 2 from the depth range of 30-70 cm.

C1-3 Soil sample taken from Chokchai District at sampling point 1 from the depth range of 70-100 cm.

All together, 21 soil samples were taken; 6 samples from Muang District, 9 samples from Pimai District and 6 samples from Chokchai District.

Table 3.1 The location of seven sampling sites.

Location (District)	**Sampling Site**	**Samples**	**Position**
Muang	1	A1-1, A1-2, A1-3	48P 0184141, UTM 1661017
	2	A2-1, A2-2, A2-3	48P 0184495, UTM 1662098
Pimai	1	B1-1, B1-2, B1-3	48P 0236892, UTM 1698233
	2	B2-1, B2-2, B2-3	48P 0235262, UTM 1699311
	3	B3-1, B3-2, B3-3	48P 0236854, UTM 1700115
Chokchai	1	C1-1, C1-2, C1-3	48P 0199885, UTM 1633476
	2	C2-1, C2-2, C2-3	48P 0199812, UTM 1625157

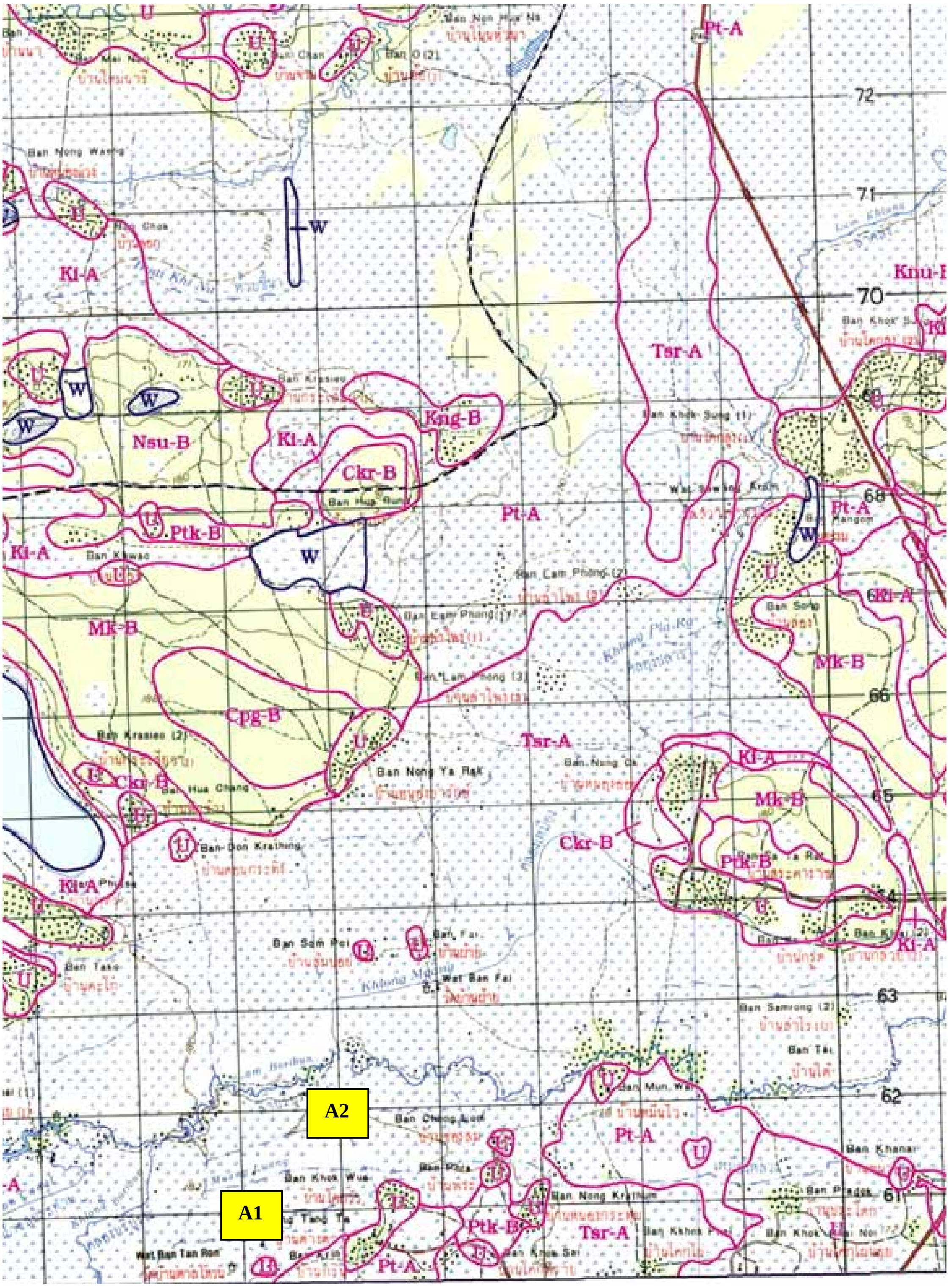


Figure 3.1 Location of the sampling areas in Muang District marked as A1 and A2.

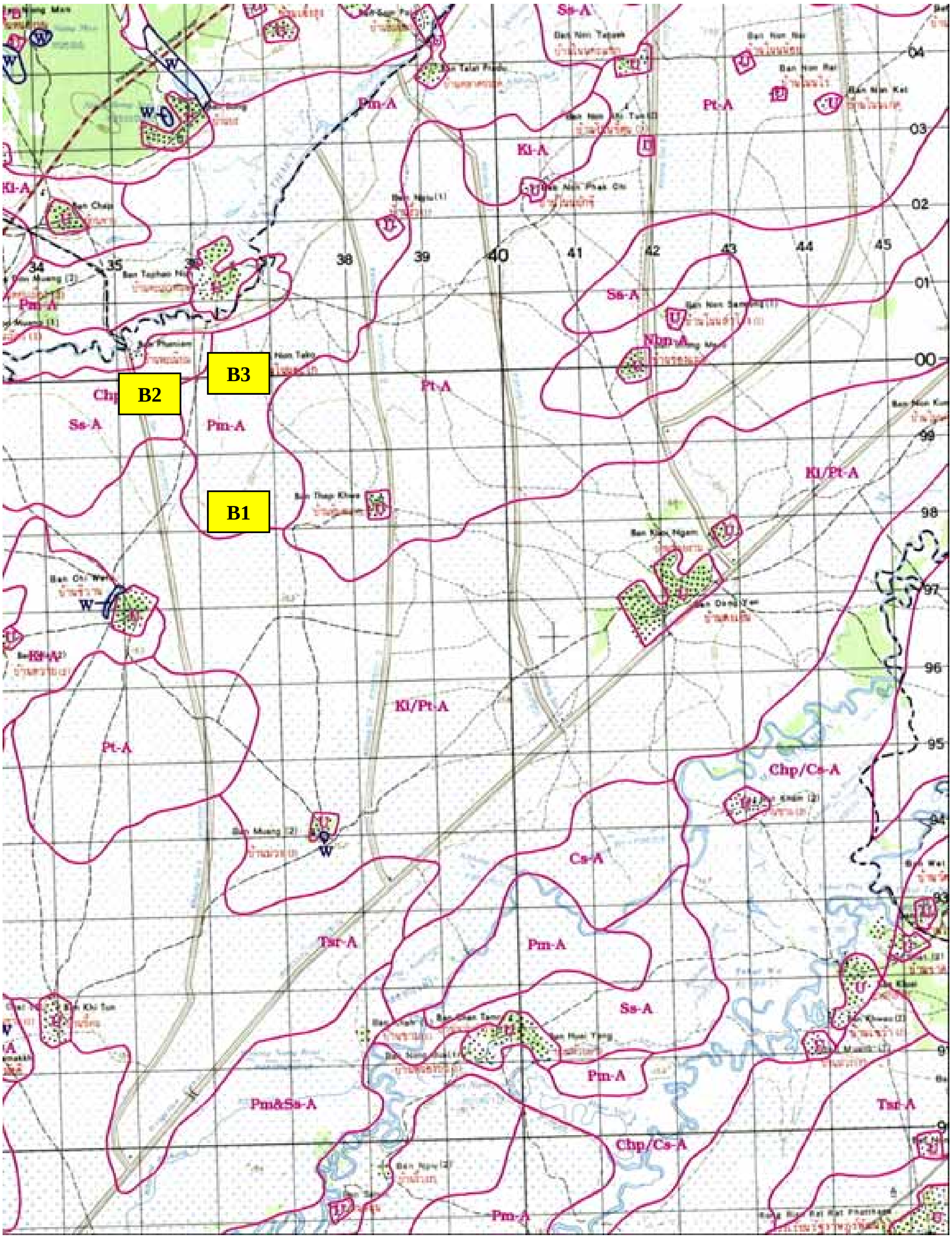


Figure 3.2 Location of the sampling areas in Pimai District marked as B1, B2 and B3.

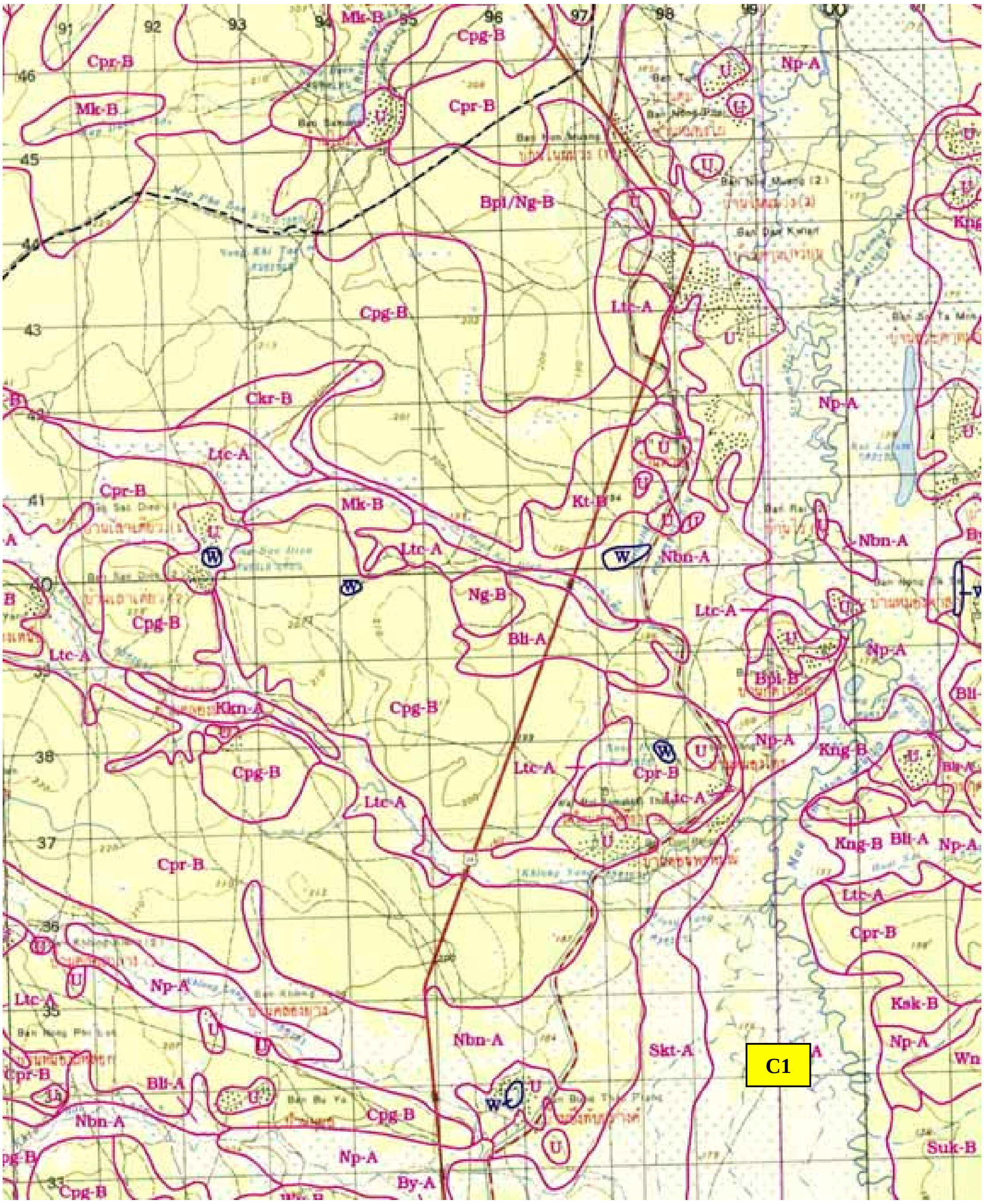


Figure 3.3 Location of the sampling area in Chokchai District: Tambol Chokchai marked as C1.

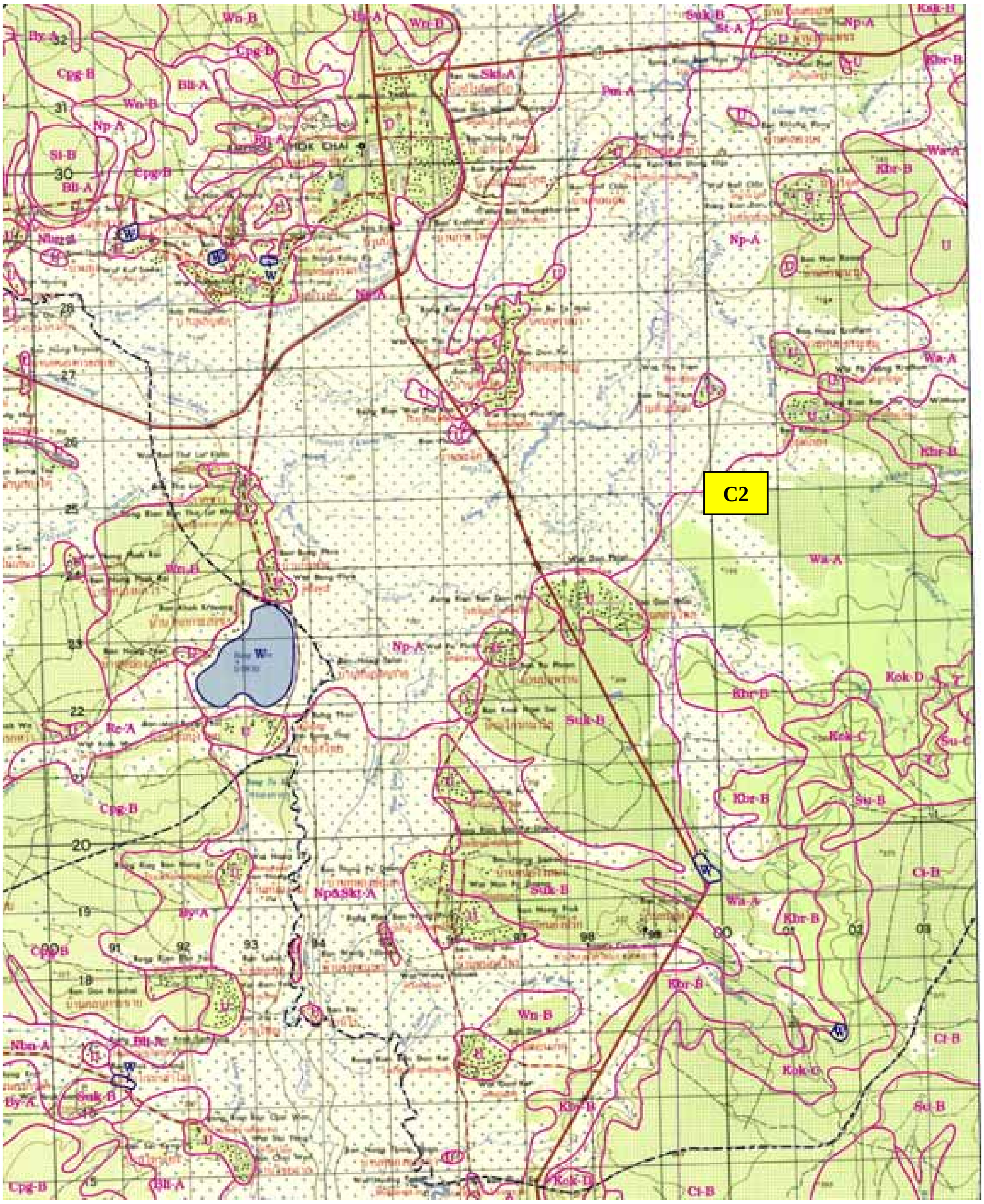


Figure 3.4 Location of the sampling area in Chokchai District: Tambol Tayiam marked as C2.

Figure 3.5 Sampling sites in Tambol Muenwai, Muang District; Ban Tanlon (A1) and Ban Natom (A2). Soil samples were collected using hand auger at 3 depth levels.

Figure 3.6 Sampling sites in Tambol Chiwan, Pimai District; Ban Nonphaniam (B1), Ban Phaniam (B2) and Ban Nontako (B3).

Figure 3.7 Sampling sites in Chokchai District; Ban Bungthapprang, Tambol Chokchai (C1) and Ban Donphlai, Tambol Tayiam (C2). Please notice the cracking of vertisol soil when dry.

3.3 Experimental methods

3.3.1 Preparation of soil samples

Soil samples were air dried by spreading the soil out on a tray in a dry and dust free room until the soil samples were dried. A sample was considered dry, when the sample weight did not change more than 5% within 24 hours.

After drying, the samples were crushed using the agate motar and passed through a 2 mm stainless steel sieve. The passage of less than 2 mm soil particles were used for all laboratory analyses (Lagen, 1996).

3.3.2 Separation of clay from soil

The extraction and dispersion of clay from soil for the purpose of mineralogical analysis are often obstructed by the presence of strongly cementing materials like carbonates and organic matter, which lead to clay aggregation. The ground soil samples required certain pretreatment before they could be analyzed by XRD. This step was to remove undesirable coatings and cements either to improve the diffraction characteristics of the samples or to promote dispersion during size fractionation. The method of dispersion in water after organic removal was used to separate clay minerals from soil. This preparation procedure comprised four steps:

- Carbonates removal by treatment with sodium acetate buffer
- Organic matter removal by oxidation with hydrogen peroxide
- Size fractionation, the 0.2 μm fraction was obtained by centrifugation method
- Flocculation of the clay dispersion by adding 1 M NaCl

3.3.2.1 Removal of carbonates

Many soils contain calcite and other soluble salts which may cement particles together and prevent their complete dispersion. The presence of carbonates inhibit proper dispersion of colloids and, thus, separation of the fine fractions (e.g.,< 5μm).

Removal of carbonates with any acid will caused a very low pH which can cause destruction of small clay particles. To prevent this, a mild treatment with sodium acetate buffer solution (pH=5) is applied.

$$CaCO_3 + 2CH_3COOH \longrightarrow CO_{2\,(g)} + H_2O + (CH_3COO)_2Ca$$

It is usual, though not essential, to remove exchangeable calcium ions or carbonate calcium as a first step. This is because calcium, if present, may precipitate as calcium oxalate during the peroxide treatment in the process of organic matter removal. Calcium oxalate would then appear in the clay fraction and interfere with identification of the components present.

Materials and equipment

1. Beakers: 600 ml
2. Water bath; Model AT110, Heto Lab equipment, Denmark
3. Glass stirring rod
4. Centrifuge bottles: 250 ml with screw caps
5. Centrifuge; Model RC28S, Sorvall, USA
6. Analytical balance; Model 3100C, Precisa, Switzerland

Reagents

1. Sodium acetate (CH_3COONa); BDH, England

   1 N sodium acetate buffer solution, pH 5.0

   Dissolved 82.03 g of CH_3COONa and 27 ml of glacial acetic acid (CH_3COOH) in water and transferred to 1 liter volumetric flask. Made up to volume with distilled water. Adjusted to pH 5.0 with acetic acid.

2. Magnesium chloride ($MgCl_2$. $6H_2O$); BDH, England

   0.5 M $MgCl_2$

   Dissolved 101.65 g $MgCl_2$. $6H_2O$ in water and transferred to 1 liter volumetric flask. Made up to volume with distilled water.

3. Hydrochloric acid (HCl) 37%; Merck, Germany

   1 M HCl

   Diluted 86 ml of concentrated HCl (37%) in about 900 ml of water and made up to volume in 1 liter volumetric flask.

Procedure

1. Weighed 20.00 g of air-dried soil into 600 ml beaker.
2. Added about 60 ml of acetate buffer solution and placed the beaker on a boiling water bath for about 30 minutes with intermittent stirring.
3. Transferred the sample into a 250 ml centrifuge bottle, after all the carbonates were removed (no more gas evolved).
4. Centrifuged and decanted the clear supernatant solution.
5. Filled up the bottle with distilled water and shaking vigorously to a well-dispersed soil suspension after that recentrifuge.

6. Decanted the clear supernatant solution. If some of the clay was still suspended, added a few drops of 1 M HCl and, if necessary, 0.5 M $MgCl_2$ to flocculate the clay and mixed the supernatant without disturbing the sedimented material. After centrifuging, decanted the clear supernatant.
7. Repeated steps 5 to 6 for washing process until all the clay were sedimented.
8. Transferred the sample with a minimum of water back into the 600 ml beaker. If necessary, allowed excess water to evaporate on a hot water bath until a volume of soil to water was 1:1 to 1:2. The sample was now ready for the removal of organic matter.

3.3.2.2 Removal of organic matter

Soil samples which contain abundant of organic matter should be treated to remove the organic compounds. Significant amounts of organic matter may also hold soil particles together and prevent the dispersion. Hydrogen peroxide is used to oxidize the colloidal and humified organic matter to provide a better dispersion of the clay-sized material after the decomposition of organometallic complexes (Douglas and Fiessinger, 1971; Kunze and Dixon, 1986; Jackson, 1979; Kimpe, 1993; Doesburg, 1996). Removal of organic matter will also preserve the crystalline Fe and Al hydroxides and oxyhydroxides. The reaction may be represented by the oxidation of a generic organic compound, such as formaldehyde (CH_2O) (Olson, Thompson and Wilson, 2000):

$$CH_2O + H_2O_2 \longrightarrow CO_2 + H_2O + 2H^+$$

Materials and equipment

1. Beakers: 600 ml
2. Centrifuge; Model RC28S, Sorvall, USA
3. Centrifuge bottles: 250 ml with screw caps
4. Glass stirring rod
5. Analytical balance; Model 3100C, Precisa, Switzerland

Reagents

1. Hydrogen peroxide (H_2O_2) 30%; Analytical Univar Reagent, New Zealand
2. 0.5 M $MgCl_2$
3. 1 M HCl

Procedure

1. Added about 15 ml of H_2O_2 (30%) to the sample which had been treated previously for carbonates removal.
2. Stirred the soil suspension occasionally and observed the reaction for about 30 minutes. If excessive frothing was present, cooled the beaker in a cold water bath. Continued adding a small amount of H_2O_2 until the sample ceased to froth.
3. Heated the sample to $70^{o}C$ in a constant-temperature water bath and observed the reaction for about 15-20 minutes.
4. Repeated adding small amounts of H_2O_2 when the reaction had ceased until the reaction was complete, i.e. the soil had lost its dark color. Generally, three additions of 10-15 ml of H_2O_2 will be sufficient to remove all organic matter.
5. Recomposed excess of H_2O_2 on a boiling water bath, after the removal of organic matter was completed. Continued heating and stirring until the release of bubbles of oxygen had stopped.

6. Transferred the sample into a 250 ml centrifuge bottle, filled up with distilled water and centrifuged.
7. Decanted the clear supernatant solution. If some of the clay was still suspended, added a few drops of 1 M HCl and, if necessary, 0.5 M $MgCl_2$ to flocculate the clay and mixed the supernatant without disturbing the sedimented material. After centrifuging, decanted the clear supernatant.
8. Filled up the bottle with distilled water and shaking vigorously to a well-dispersed soil suspension after that centrifuged to wash the sample.
9. The washed samples, free of carbonates and organic matter, were ready for the separation of the clay fraction.

3.2.2.3 Size fractionation

The dispersed sample was wet sieved through a 325 mesh sieve (45 μm) to separate very fine sand (Figure 3.8). The centrifuge method was then used to separate other fine (clay and silt) fractions.

In this experiment, the fine clay fraction (0.2 μm) was isolated by centrifuge method. The centrifugation time was calculated from the following equation based on Stoke’s law (Sheldrick and Wang, 1993; Department of Land, Air & water Resource (LAWR), UCDAVIS, www, 2004).

$$t_{min} = \frac{63.0 \times 10^{8}\, n \log R/S}{N_m^{2}\, D_\mu^{2}\, \Delta s}$$

Where t_{min} is the time for sedimentation in minutes, n is the viscosity of water in poises, R is the radius of rotation of the top of the sediment in centimeters, S is the radius of rotation of the surface of the suspension in centimeters (Figure 3.9). N_m is the speed of the centrifuge in rpm, D_μ is the particle diameter in microns and Δs is the difference in specific gravity between the solvated particle and the suspension liquid. When *n* is 0.00894 (25°C), R is 14.1 cm, S is 8.1 cm, N_m is 2500 rpm, Δs is 1.503, the centrifugation time needed to sediment all soil particles larger than 0.2 µm was 36 minutes.

45 µm sieve openings (325 mesh per inch)

Suspension of particle size less than 45 µm in diameter (silt and clay)

Figure 3.8 Apparatus for wet-sieving of dispersed soil suspension to effect the 45 µm separation.

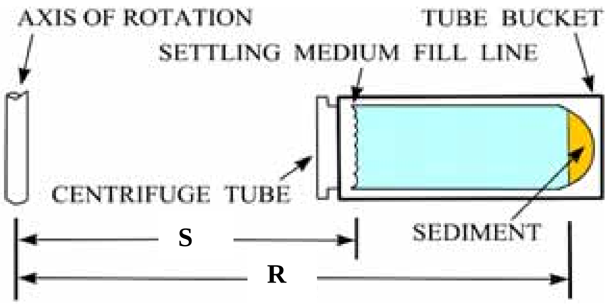


Figure 3.9 Diagram showing R and S distances from the axis of rotation.

Materials and equipment

1. Sieve: 325 mesh (45 µm)
2. Beakers: 1000 ml
3. Centrifuge; Model universal 30 RF, Hettich, Germany
4. Centrifuge bottles: 125 ml with screw caps
5. Shaker; Model GFM 3006, Germany
6. 25 cm diameter glass funnels and stand

Procedure

1. Added distilled water to the centrifuge bottles that contained samples which were free of carbonates and organic matter and shook the bottles for 12 hours to disperse.
2. Sieved the suspension on a 325 mesh sieve placed above the funnel. Collected the filtrate in a 1 liter beaker.
3. Discarded the sand left on a 325 mesh sieve.
4. Filled the beaker with distilled water and mixed thoroughly.
5. Marked the centrifuge bottles to indicate levels S and R (Figure 3.9) before centrifuged, and then filled the centrifuge bottles with soil suspension from the beaker to the level marked S. Mixed the suspension well, and centrifuged at 2500 rpm for 36 minutes to sediment particles coarser than 0.2 µm to the level lower than R.
6. Removed the suspension between level R and S by siphoning, and stored this suspension in a large beaker.
7. Repeated steps 4 through 6 (processes of adding water, mixing and centrifugation) until the supernatant was clear.

3.3.2.4 Flocculation

A complete 0.2 μm clay suspension would result in large volumes and was often necessary to concentrate the suspension for further use. The flocculation of colloid was usually accomplished by adding metal chloride (NaCl, $MgCl_2$ or $CaCl_2$). The clear supernatant was then siphoned off. In this work 1 N NaCl was used to flocculate the clay suspension (Whittig and Allardice, 1986; Moore and Reynolds, 1997).

Materials and equipment

1. Hot plate; Schott, Germany
2. Oven; Model 400, Memmert, Germany
3. Centrifuge; Model RC28S, Sorvall, Germany
4. Centrifuge bottles; 250 ml with screw caps
5. Watch glass

Reagents

1. Sodium chloride (NaCl); Merck, Germany

   1 M NaCl

   Dissolved 58.44 g NaCl in water and transferred to 1 liter volumetric flask. Made up to volume with distilled water.

2. Silver nitrate ($AgNO_3$)

   0.1 N $AgNO_3$

   Dissolved 1.69 g $AgNO_3$ in water and transferred to 100 ml volumetric flask. Made up to volume with distilled water.

3. Methanol 95%

Procedure

1. Added sufficient 1 M NaCl to 0.2 µm clay suspension to sediment all Na-montmorillonite.
2. Let the suspension stood until the clay flocculated and settled**,** removed the clear supernatant liquid with a siphon.
3. Transferred the flocculated clay to 250 ml centrifuge tubes, and centrifuged to sediment Na-montmorillonite. Decanted the supernatant liquid.
4. Added 1 M NaCl to centrifuge bottles that contained sedimented Na-montmorillonite and shook the bottles for 12 hours to disperse.
5. Centrifuged the suspension and decanted the clear supernatant.
6. Repeated step 4 to 5, to ensure full saturation of the exchangeable sites with Na.
7. Washed the clay with methanol to remove the excess salt until there was no chloride. Tested the supernatant to make sure it was Cl^- free with a few drops of 0.1 N $AgNO_3$.
8. Dried the Na-saturated clay at $60^{o}C$ for 48 hours and stored in polyethylene containers.
9. Calculated the percentage of Na-clay.

Calculation

The percentage of Na-clay was calculated using the following equation.

$$\text{Na-clay (\%)} = \frac{\text{Na-clay (dry)} \times 100\%}{\text{Soil sample used}}$$

3.3.3 Modification of montmorillonite

Organoclay, the montmorillonite modified by alkylammonium ions, has found a wide application in industry. Modification of montmorillonite was attempted in this research. Montmorillonite is naturally hydrophilic. This makes it poorly suited to mixing and interacting with most polymer matrices. Moreover, the stacks of clay platelets are held tightly together by electrostatic forces. For these reasons, the clay must be treated before it can be used to make nanocomposites (Department of Polymer Science, University of Southern Mississippi, www, 2005).

Modification of the clay surface is made by replacing the native exchangeable inorganic cations with organic cations. When the interlayer metal cations are replaced with organic cations (e.g. alkylammonium ion), the surfaces of the clay are greatly modified and become organophilic. The replacement of inorganic exchangeable cations by organic cations determines the degree of expansion of the clay galleries. The hydrophilic character of the clay surface is changed to hydrophobic, and the intercalation into the gallery space of the precursor organic molecule is facilitated (Prost and Yaron, 2001).

In this work, 1-hexadecylamine ($C_{16}H_{35}N$) was used to organically modify montmorillonite (Xiao, Zhan and Li, 2003). The reagent was the courtesy of Assistant Professor Dr. Visit Vao-soongnern, the School of Chemistry, Suranaree University of Technology, who is now working on nanocomposites. The modified montmorillonite would be further studied by his research group.

Materials and equipment

1. Shaker with thermostated water bath; Model SWB5050, National Labnet, Denmark
2. Erlenmeyer flasks: 100 ml
3. Oven; Model 400; Memmert, Germany
4. Suction and filter papers no. 1; Whatman, England

Reagents

1. Ethanol 95%; Italma (Thailand) Co.,Ltd.
2. 1-Hexadecylamine 90%; Sigma Aldrich, Germany
3. Hydrochloric acid 37%; Merck, Germany
4. 0.1 N $AgNO_3$

Procedure

1. Added 25 ml 95% ethanol and 25 ml distilled water to a 100 ml Erlenmeyer flask, then put in a thermostated shaking water bath.
2. Added 5.00 g of Na-montmorillonite into the flask, intensely shook for 1 hour to disperse the sample evenly.
3. Heated the flask up to 80^{o}C.
4. Introduced 0.01 mol hexadecylamine and the same amount of HCl into the flask, started timing, continued shaking for 3 hours, took the samples out of the bath.
5. Filtered the samples immediately after taken out, and washed by solution of water and 95% ethanol (1:1 volume ratio) for several times until no white precipitates (AgCl) were observed when added several drops of 0.1 N $AgNO_3$ into the filtrate, which meant that no chloride existed in the samples.
6. Dried the samples at 70^{o}C for 48 hours.

3.4 Instrumentation for mineralogical analysis

3.4.1 X-ray diffraction spectrometer

The X-ray diffraction analysis was undertaken to investigate qualitatively the composition of the clay mineralogy in the soil samples. It is important to identify clay minerals, for example, montmorillonite, kaolinite, illite and chlorite, etc., as they may influence the behavior and properties of the clay materials. The cation exchange capacity, specific surface area, plasticity, and retention capability are very much dependent on clay mineralogy.

Clay minerals are phyllosilicates and maximum information will be obtained from XRD patterns of preferentially oriented specimens showing specific variations of d001-spacings, i.e., specific spacings of basal reflections. This behavior depends largely on the nature of the cations present on the excite exchangeable sites.

Sample preparation

The glass slide method was used in this study because of its ease of handling and small amount of samples were needed. The sample was suspended in water and dispersed onto the glass slide (Figure 3.10). The slide was dried , giving a preferred orientation of the clay mineral platelets parallel to the slide. The clay samples were being run under three separate conditions; Na-saturated, Mg-saturated, and Mg-saturated with glycerol treatment (Whittig and Allardice, 1986; Kimpe, 1993).

Figure 3.10 The clay samples prepared for XRD by glass slide method.

Materials and equipment

1. X-ray diffraction spectrometer; D5005 X-ray, Bruker, Germany
2. Centrifuge; Model Labofuge 200, HERAEUS SEPATECH
3. Glass slides; 25 x 30 mm
4. Vortex Mixer; VM-300, Taiwan
5. Oven; Model 400; Memmert, Germany
6. Test tubes: 5, 10 ml

Reagents

1. Magnesium chloride ($MgCl_2$. $6H_2O$); BDH Laboratory Supplies, England

   1 M $MgCl_2$

   Dissolved 203.30 g $MgCl_2$. $6H_2O$ in water and transferred to 1 liter volumetric flask. Made up to volume with distilled water.

2. Glycerol ($C_3H_8O_3$); BDH Laboratory Supplies, England

   Glycerol solution

Pipetted 1.00 ml of glycerol and transferred to 100 ml volumetric flask and made up to 100 ml with ethanol.

Slide preparation

1. Na-saturated clay slide

Procedure

1. Weighed 30 mg of the Na-saturated clay into a 5 ml tube.
2. Added 1 ml of distilled water and mixed thoroughly with a Vortex Mixer.
3. Spreaded the suspension on a clean glass slide.
4. Let the sample air-dried on a horizontal surface to ensure even distribution of the particles.

2. Mg-saturated clay slide

Procedure

1. Weighed 30 mg of Na-saturated clay into a 10 ml centrifuge tube
2. Added 7 ml of 1 M $MgCl_2$ solution. Mixed thoroughly with a Vortex mixer.
3. Centrifuged and discarded the supernatant.
4. Repeated step 2 to 3, twice to ensure full saturation of the exchangeable sites with Mg.
5. Washed the sample with distilled water after the exchange was completed, centrifuged, and discarded the supernatant. Washed until the supernatant was Cl^- free.
6. Added 1 ml of distilled water and mixed thoroughly.
7. Spreaded the suspension on a clean glass slide.
8. Let the sample air-dried on a horizontal surface to ensure even distribution of the particles.

3. Mg-saturated clay with glycerol treatment

Procedure

1. Proceeded as preparing the Mg-saturated clay slide.
2. Added dropwise, at several places on the slide, 0.4 ml of 2% glycerol in ethanol solution and let it air-dried.

The slides were examined by a Bruker D5005 X-ray diffractometer with monochromat, CuKα radiation using 40 kV and 40 mA. Spectra were collected from 3^{o} to 35^{o} 2θ in 0.02^{o} steps, counting for 1^{o} per minute.

3.4.2 Fourier transform infrared spectroscopy

FTIR will provide the information about the nature and identity of compounds that may be amorphous to X-ray; IR technique will help in identifying inorganic compounds, minerals which have well-defined absorption bands.

A Perkin-Elmer GX FTIR Spectrometer, were used to take the mid IR spectra of samples (4000-400 cm^{-1}) with the KBr pellet technique (Kloprogge et al., 2002).

Materials and equipment

1. Fourier transform infrared spectrometer; FTIR spectrometer, Spectrum GX, Perkin-Elmer, Germany
2. Agate mortar and pestle
3. Hydraulic pressing machine

Reagents

KBr powder; Sigma Aldrich, Germany

Procedure

1. Dried the KBr powder at 120°C for 1 h before used.
2. Mixed approximately 1 mg each of Na-saturated clay sample with 250 mg KBr powder and ground to very fine powder with agate mortar and pestle.
3. Pressed the ground powder into a transparent disk using a hydraulic pressing machine with an equivalent weight of about 10 tons for 1 minute.
4. Obtained the spectra using an average of 10 scans with 4 cm^{-1} resolution.

3.4.3 Transmission electron microscope

Clay fractions were prepared for a TEM study by dispersing the sample in distilled water. The samples were placed on a formvar-coated TEM grid and examined with TEM (Suthiprakarn, 1991).

Materials and equipment

1. Transmission electron microscope; JEM 2010, JEOL, Japan
2. Copper 200 mesh grid; SPI Supplies
3. Vortex Mixer; VM-300, Taiwan

Procedure

1. Weighed 5 mg of Na-saturated clay into a 15 ml tube.
2. Added 10-15 ml of distilled water and dispersed the sample thoroughly with a Vortex Mixer.
3. Added the clay suspension dropwise on a formvar-coated TEM grid (200 mesh).
4. Air-dried the sample and examined with TEM.

3.4.4 Scanning electron microscope

The morphology of the montmorillonite particles was examined by JEOL scanning electron microscope. The powdered samples were dispersed in distilled water and, following the sedimentation on a brass stub, it was coated with gold in an ionization chamber. Morphology of the solid sample could be seen through the use of SEM. Crystal shape and size of the crystalline solid phase could be identified from the micrograph. The sample for the SEM observation was prepared according to Suthiprakarn (1991).

Materials and equipment

1. Scanning electron micrope; JSM 6400, JEOL, Japan
2. Brass stub
3. Balzer sputtering coater; JFC-1100E, JEOL, Japan

Procedure

1. Weighed 5 mg of Na-saturated clay into a 15 ml tube.
2. Added 10-15 ml of distilled water and dispersed thoroughly with a Vortex Mixer.
3. Added the clay suspension dropwise on a brass stub sample holder.
4. Air dried the sample then coated the sample with a layer of gold using a Balzer sputtering coater. The various magnification were used to obtain suitable micrographs of clay samples.

3.4.5 Thermal analysis: simultaneous DSC-TGA instrument.

The sodium saturated clay thermal behavior was studied with a thermal analysis system using simultaneous DSC-TGA model SDT2960 series instrument. Experiments were performed under constant nitrogen flow with a heating rate of 20^{o}C min^{-1}. Alumina powder was used as a reference material during the determination. Approximately 20 mg samples of Na-saturated clay was packed into alumina sample pans.

Materials and equipment

1 Thermal analysis: simultaneous DSC-TGA instrument; SDT2960, TA-Instruments, New Castle (DE), USA

2 Nitrogen gas, 99.99% purity; TIG, Thailand

3 Spatula

4 Analytical balance; Model 205A, Precisa, Switzerland

5 Alumina pan: 90 µl

Reagents

Alumina powder; Sigma Aldrich, Germany

Procedure

1 Set-up the instrument. Select operating mode "TGA-DTA" to run the SDT with both weight change and temperature difference for samples and cell constant calibration.

2 Turned on the N_2 purge gas and set to 100 cm^3 min^{-1} sample purge.

3 Entered the information into thermal advantage program.

4 Placed the alumina reference pan that contained reference material, Al_2O_3 powder and empty alumina sample pan onto the platforms and then closed the furnace. Tared the sample and reference pan.

5 Opened furnace, removed the sample pan from the platform. Weighed about 20 mg of Na-saturated clay sample into the sample pan.

6 Used flat-tipped forceps to tap the sample pan against a hard surface several times to uniformly distribute the sample.

7 Carefully placed the sample pan onto the platform.

8 Run the sample heating program with a heating rate of 20°C min^{-1}, starting temperature at 30°C, and ending temperature at 1000°C.

9 Started immediately the "Run" program.

10 Removed the sample and reference pan from the platforms after finished the run and SDT cool.

11 Opened furnace, got the sample pan out to balance arms of furnace.

12 Analyzed the result by using the universal analysis program.

3.4.6 Wavelength dispersive X-ray fluorescence

WDXRF was used to determine the elemental compositions of soil samples. In this work, XRF (Phillip, MagiX Pro) was used to measure the composition of clay fraction. The samples were prepared for the measurement by using lithium borate-fusion technique. This mixture was heated to about 1000°C. At this temperature, the flux melted and the samples were dissolved to form a perfectly homogeneous mass. Finally, the molten material was cast to form a glass disk to be analyzed by XRF. When the glass disks were made for XRF analysis, a small amount of non-wetting agents were added to allow for easy removal of the glass disk from the platinum mould. The use of a non-wetting agents was essential. Lithium bromide (LiBr) is an excellent non-wetting agent.

The XRF analysis was being done by the National Metal and Material Technology Center (MTEC).

3.5 Particle size determination by laser diffraction

Laser diffraction is a technique used for the analyzing of the grain-size distribution of a core sample. A cleaned, disaggregated sample is dispersed in a carrier fluid. The grains caused diffraction of a laser beam directed through the fluid. The angle of scattering is inversely proportional to the particle size, while the intensity of scattering is proportional to the number of particles (Schulmberger Limited, www, 2005).

In this work, the laser diffraction particle analyzer of Malvern Instruments (Mastersizer S Ver. 2.15) was used for the analysis. The parameters of the instrument were shown in Table 3.2 (Malvern Instruments Limited, 1995). Results of laser diffraction measurements were in volume percentages of the fractions. If the bulk density of the particles in various size ranges was similar, the volume fractions would be equal to the mass fractions.

Sample preparation for laser grain sizing was made as follows: the small subsamples were treated with peroxide to remove organic matter, and sonicated. Some samples might be treated with HCl to remove $CaCO_3$, or with sodium dithionite to remove free iron and manganese. So that the particles would be well dispersed in an aqueous solution (Pape, 1996).

Table 3.2 Parameters details of laser particle size analysis of Malvern Instruments (Mastersizer S Ver. 2.15).

Parameters	**Details**
Range Lens	300RF (0.05-900 μm)
Presentation	3OHD [Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]
Analysis Model	Polydisperse
Beam length	2.40 mm
Obscuration	10-30%
Sampler	MS17

Materials and equipment

1. Laser diffraction particle analyzer, Mastersizer S Ver. 2.15, Malvern Instruments, England
2. Water bath; Model AT110, Heto Lab equipment, Denmark
3. Glass stirring rod
4. Centrifuge bottles: 250 ml with screw caps
5. Centrifuge; Model RC28S, Sorvall, USA
6. Analytical balance; Model 3100C, Precisa, Switzerland

Reagents

1. Sodium citrate/bicarbonate solution

   Dissolved 88.00 g of sodium citrate ($C_6H_5Na_3O_42H_2O$) and 8.40 g of sodium hydrogencarbonate ($NaHCO_3$) in 1 liter water.

2. Sodium chloride solution, saturated

   Dissolved 325.00 g of sodium chloride (NaCl) in 1 liter water.

3. Sodium dithionite; Fluka Chemical, Germany
4. Acetone 99%; Mallinckrodt Chemical, USA

Procedure

1. Removed carbonates and organic matter as in 3.3.2.1 and 3.3.2.2.
2. Added 100 ml of sodium citrate/hydrogencarbonate solution to the samples free of carbonates and organic matter from 3.3.2.1 and 3.3.2.2 to remove iron oxide. Jarred the soil loose from the walls.
3. Warmed the soil suspension to 75°C by placing the centrifuge bottles in the openings of a hot water bath. Avoided heating above 80°C because of the risk of forming insoluble FeS or elemental S.
4. Added about 2 g of sodium dithionite powder, using a spoon or spatula, and stirred the suspension constantly for one minute and then occasionally during the next 10 minutes. Then added a second 2 g portion of sodium dithionite and stirred.
5. Took the bottles away from the water bath and observed the soil suspension. If the suspension failed to flocculate within 5 minutes, added 25 ml of a saturated NaCl solution and, if necessary, 10 ml of acetone. Mixed the suspension and warmed it to promote flocculation. Balanced pairs of bottles and centrifuged.
6. Extracted the clear supernatant liquid using a water jet pump or decantation. Repeated steps 1 to 4 if a reddish-brown color of the soil indicated that the removal of iron oxides was still incomplete.
7. When completed, washed the samples two or more times with water until the yellow-brown color of the iron citrate complex had disappeared. If necessary for flocculation, washed with 1M NaCl and warmed the suspension on a water bath before centrifuging.

8. After the washing was completed, the sample was freed of carbonates, organic matter and iron oxides.
9. Removed the sand by wet sieved. The clay fraction sample was ready for the particle size distribution analysis by laser diffraction.

CHAPTER IV

RESULTS AND DISCUSSION

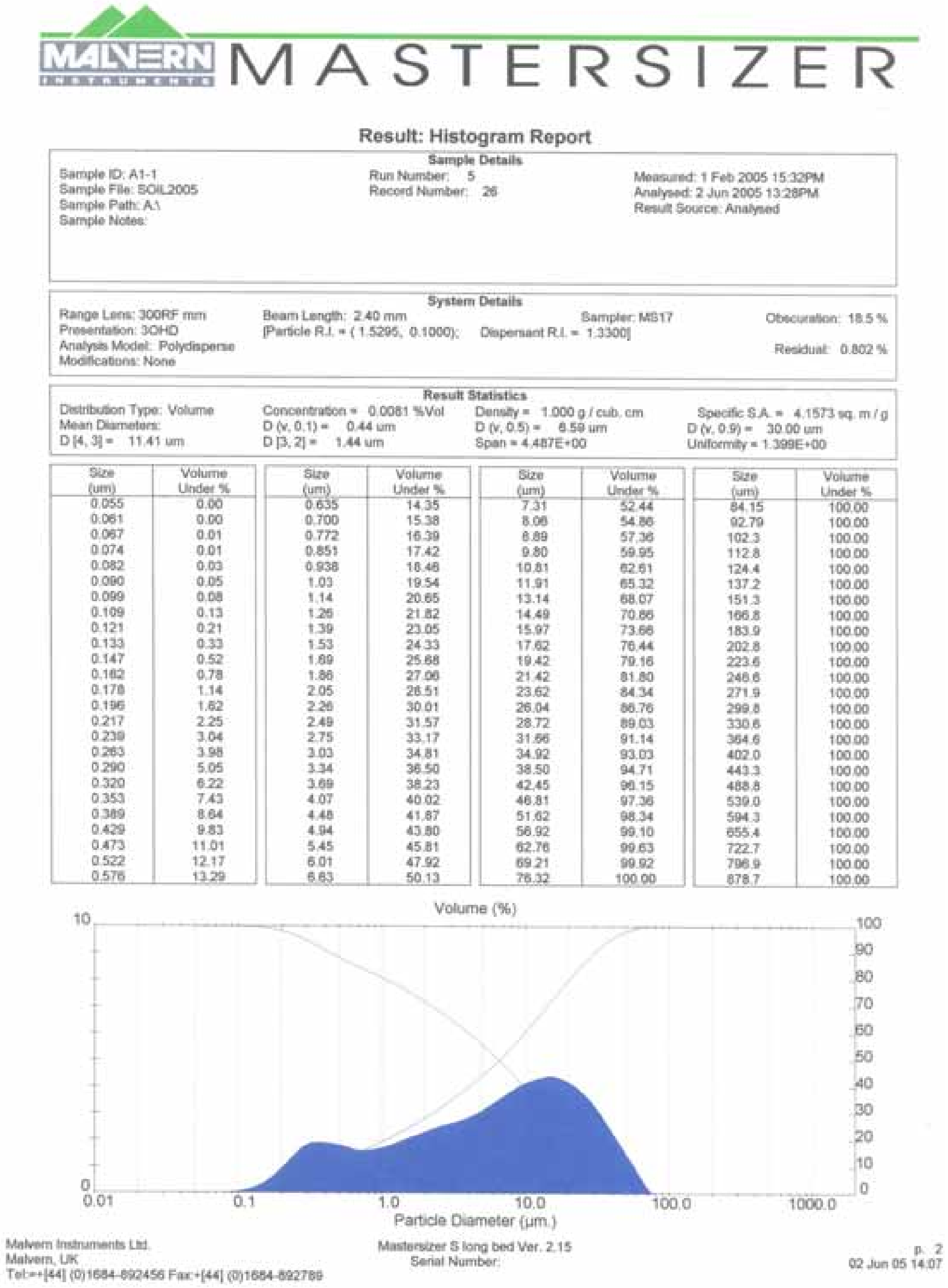
The experimental results are discussed in this chapter. Firstly, the results of particle size distribution of clay in soil are reported. Secondly, the semiquantitative analysis for the separated fine clay (< 0.2 μm) is shown. Thirdly, the characterization results for the separated fine clay are shown and discussed. Finally, the characterization results of modified clay obtained from the separation are demonstrated.

4.1 Particle size distribution of clay in soil

The percentages distribution of clay fraction of the soil samples were determined by laser particle size distributions analysis. In fact, the clay-sized particles were smaller than 2 μm but the results obtained from the analyzer were reported as 2.05 μm. So the results shown in Table 4.1.

From the results, soil samples contained between 28.51-73.63% clay, the majority of which were higher than 30% clay. The different of depth do not affect the clay contents except the soil samples from site 1, Muang District and from site 1, Pimai District in which the percentages of clay increased as the depth increased.

Figure 4.1 shows the example of laser diffraction size distribution analysis.



MALVERN INSTRUMENTS MASTERSIZER

Result: Histogram Report

Sample Details

Sample ID: A1-1
Sample File: SOIL2005
Sample Path: A:\
Sample Notes:

Run Number: 5
Record Number: 26

Measured: 1 Feb 2005 15:32PM
Analysed: 2 Jun 2005 13:28PM
Result Source: Analysed

System Details

Range Lens: 300RF mm
Presentation: 3OHD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: MS17

Obscuration: 18.5 %
Residual: 0.802 %

Result Statistics

Distribution Type: Volume
Mean Diameters:
D [4, 3] = 11.41 um

Concentration = 0.0081 %Vol
D (v, 0.1) = 0.44 um
D [3, 2] = 1.44 um

Density = 1.000 g / cub. cm
D (v, 0.5) = 6.59 um
Span = 4.487E+00

Specific S.A. = 4.1573 sq. m / g
D (v, 0.9) = 30.00 um
Uniformity = 1.399E+00

Size (um)	Volume Under %	Size (um)	Volume Under %	Size (um)	Volume Under %	Size (um)	Volume Under %
0.055	0.00	0.635	14.35	7.31	52.44	84.15	100.00
0.061	0.00	0.700	15.38	8.06	54.86	92.79	100.00
0.067	0.01	0.772	16.39	8.89	57.36	102.3	100.00
0.074	0.01	0.851	17.42	9.80	59.95	112.8	100.00
0.082	0.03	0.938	18.46	10.81	62.61	124.4	100.00
0.090	0.05	1.03	19.54	11.91	65.32	137.2	100.00
0.099	0.08	1.14	20.65	13.14	68.07	151.3	100.00
0.109	0.13	1.26	21.82	14.49	70.86	166.8	100.00
0.121	0.21	1.39	23.05	15.97	73.66	183.9	100.00
0.133	0.33	1.53	24.33	17.62	76.44	202.8	100.00
0.147	0.52	1.69	25.68	19.42	79.16	223.6	100.00
0.162	0.78	1.86	27.06	21.42	81.80	246.6	100.00
0.178	1.14	2.05	28.51	23.62	84.34	271.9	100.00
0.196	1.62	2.26	30.01	26.04	86.76	299.8	100.00
0.217	2.25	2.49	31.57	28.72	89.03	330.6	100.00
0.239	3.04	2.75	33.17	31.66	91.14	364.6	100.00
0.263	3.98	3.03	34.81	34.92	93.03	402.0	100.00
0.290	5.05	3.34	36.50	38.50	94.71	443.3	100.00
0.320	6.22	3.69	38.23	42.45	96.15	488.8	100.00
0.353	7.43	4.07	40.02	46.81	97.36	539.0	100.00
0.389	8.64	4.48	41.87	51.62	98.34	594.3	100.00
0.429	9.83	4.94	43.80	56.92	99.10	655.4	100.00
0.473	11.01	5.45	45.81	62.76	99.63	722.7	100.00
0.522	12.17	6.01	47.92	69.21	99.92	796.9	100.00
0.576	13.29	6.63	50.13	76.32	100.00	878.7	100.00

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Figure 4.1 Results of laser diffraction measurement are in volume percentages of fraction.

Table 4.1 The percentages distribution of clay fraction of the soil samples from the laser particle size distributions analysis.

Location (District)	Site	Sample	Depth (centimeters)	Percentages of clay (2.05 μm)
Muang	1	A1-1	0-30	28.51
		A1-2	30-70	36.37
		A1-3	70-100	43.08
	2	A2-1	0-30	52.87
		A2-2	30-70	53.02
		A2-3	70-100	51.14
Pimai	1	B1-1	0-30	56.44
		B1-2	30-70	61.55
		B1-3	70-100	73.63
	2	B2-1	0-30	55.71
		B2-2	30-70	67.51
		B2-3	70-100	68.98
	3	B3-1	0-30	38.12
		B3-2	30-70	53.69
		B3-3	70-100	42.65
Chokchai	1	C1-1	0-30	33.81
		C1-2	30-70	35.61
		C1-3	70-100	33.20
	2	C2-1	0-30	45.42
		C2-2	30-70	38.63
		C2-3	70-100	38.88

4.2 Semiquantitative of the separated fine clay

The separation of clays from soil required sample pretreatment, removal of carbonates and organic matter, to promote dispersion during clay size fractionation. Since the smectite series were more resistant to chemical weathering and tend to persist in greater quantities in the finer clay fractions, attempts had been made to separate the fine clay (< 0.2 μm) by centrifugation technique. The fine clay fraction was then saturated with Na^+ using 1 M NaCl. Sodium ion will maintain the dispersion of clay particles. The percentages of the fine clay obtained are calculated as Na-clay and shown in Table 4.2. Figure 4.2 shows the character of the separated Na-clay. For XRD analyses, Na ions at cation exchange sites of dispersed clay were replaced by Mg ions.

Table 4.2 The percentages of the Na-clay after separated from soil samples.

Location (District)	Site	Sample	Depth (centimeters)	Percentages of the Na-clay (< 0.2 µm)
Muang	1	A1-1	0-30	31.97
		A1-2	30-70	35.25
		A1-3	70-100	38.73
	2	A2-1	0-30	49.37
		A2-2	30-70	47.32
		A2-3	70-100	49.68
Pimai	1	B1-1	0-30	58.75
		B1-2	30-70	62.85
		B1-3	70-100	65.50
	2	B2-1	0-30	57.45
		B2-2	30-70	62.15
		B2-3	70-100	68.32
	3	B3-1	0-30	34.47
		B3-2	30-70	33.55
		B3-3	70-100	34.65
Chokchai	1	C1-1	0-30	36.23
		C1-2	30-70	30.05
		C1-3	70-100	28.88
	2	C2-1	0-30	36.67
		C2-2	30-70	37.43
		C2-3	70-100	31.09

Figure 4.2 The character of the separated Na-clay.

4.3 Chemical composition analysis

The chemical compositions of the Na-clay samples determined by WDXRF are reported in Table 4.3. The major components of the fine clay samples are oxides of Si and Al. The amounts of Fe_2O_3, are derived from the crystalline lattice of illite, which contains about 4-6% of Fe_2O_3, and from the clay minerals of the smectite group, that is, montmorillonite or members from the series nontronite-beidellite, according to Santos (1989). The sample A1-1, B1-3 and C1-2 have high contents of Al_2O_3, Fe_2O_3 and K_2O as compared with Na-montmorillonite (SWy-2). But the SiO_2 , MgO and CaO contents of the samples are low, as compared with commercial montmorillonite (SWy-2).

Table 4.3 The chemical compositions of certain Na-clay samples by WDXRF. Results from the National Metal and Material Technology Center (MTEC).

Chemical content (%weight)	Sample A1-1	Sample B1-3	Sample C1-2	Na-MMT (SWy-2)
SiO_2	54.525	54.646	52.768	62.900
Al_2O_3	29.208	31.951	30.478	19.600
Fe_2O_3	10.203	7.900	10.242	3.350
MgO	1.530	1.048	1.374	3.050
Na_2O	1.965	1.806	1.525	1.530
CaO	0.0460	0.0680	0.0270	1.680
K_2O	2.004	0.794	2.390	0.530
TiO_2	0.412	0.627	0.489	0.090

4.4 Clay minerals identification

The mineralogical data obtained through the X-ray diffraction analysis, thermal analysis, infrared analysis,TEM and SEM would be discussed individually and then an integration of all the data were presented.

4.4.1 X-ray diffraction

XRD is the most efficient and effective method to identify clay minerals that are present in soil. In general, no two minerals have exactly the same distances between planes of atoms; therefore, diffraction angles and patterns of angles are distinctive for individual minerals.

Layer silicates differ from one another primarily in the z-dimension. So, unlike most other minerals, layer silicates are often identified by X-ray analyses of samples that are oriented to emphasize those differences. Well oriented samples can be produced by sedimenting a suspension of clay onto a glass microscope slide. In addition, d-spacings that are perpendicular to the basal plane of atoms change in response to saturation with different cations, intercalation with organic compounds, and heating. From these properties, layer silicate minerals can be identified from the sample XRD pattern.

The diagnostic diffraction spacings of layer silicates and other common minerals present in the soil are summarized in Tables B1-B3, Appendix B (Jackson, 1965; Whittig and Allardice, 1986).

Representative X-ray diffractograms of the separated fine clays are shown in Figures 4.3-4.9 and the results of the X-ray diffraction analyses of these soils are shown in Table 4.4.

The X-ray diffraction data consistently indicate the presence of predominant amount of montmorillonite with moderate amounts of kaolinite and illite and traces of quartz.

Montmorillonite is identified in all soil samples. It is represented by a basal (001) reflection at 11-12 Å for the Na-saturated clay (Figures 4.3-4.4 and Figure 4.5 (a)), at 14-15 Å for Mg-saturated clay, and increased to 17-19 Å after glycerol solvation (Figures 4.6-4.7), which proves that the separated clay fraction is really montmorillonite not the similar 2:1 layer group of vermiculite, a non-swelling 2:1 layer silicates

Kaolinite is also identified in all soil samples. It is identified by a basal (001) reflection at 7.1-7.2 Å and (002) reflection at 3.53 Å (Figures 4.3-4.5). On solvation with glycerol, kaolinite is essentially nonexpanding.

Illite is positively identified in two locations, Muang District and Chokchai District (Figure 4.3 and Figure 4.5). Illite is represented by its basal reflections at 10.1 Å, 4.98-5.01 Å and 3.33 Å.

Quartz forms one of the traces abundant of minerals in most of the samples. Quartz is identified by its distinctive reflections at 4.26 and 3.35 Å, the peak of quartz show in Figure 4.3, Figures 4.4 (a) and (b). But in some samples there is a coinciding with (003) reflection at 3.33 Å peak of illite, which makes it difficult to use 3.35 Å peak to identify the present of quartz mineral. The sample must have reflections at 4.26 Å also, to confirm of quartz.

Illite-montmorillonite mixed layer clay is identified in sample C2-1, C2-2 and C2-3 from Chokchai District. It is identified by a basal (001) reflection at 10 Å for Na-saturated sample and 15 Å for the Mg-saturated sample. Both 10 and 15 Å peaks are quite broad but will separate into 2 peaks (Figure 4.8) after glycerol solvation. The first peak at 10 Å is from illite and the second peak at 17-19 Å is obtained from the expansion of the basal spacings of montmorillonite. So this phenomenon confirms the present of illite-montmorillonite (I/M) mixed layer clay (Moore and Reynolds, 1997).

Figure 4.9 show XRD patterns of the Na-clay samples at 0-30 cm depth. From this figure show that XRD patterns are similarity.

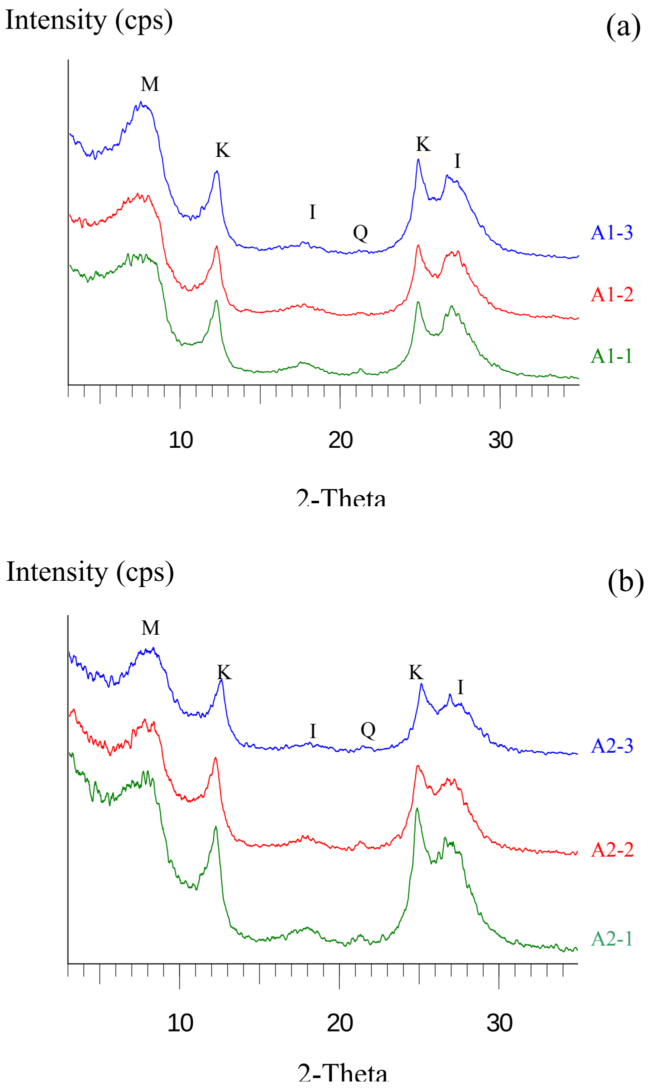


Figure 4.3 XRD patterns of the Na-clay samples at three different depths; (a) sample A1 and (b) sample A2. (M: Montmorillonite, K: Kaolinite, I: Illite, Q: Quartz)

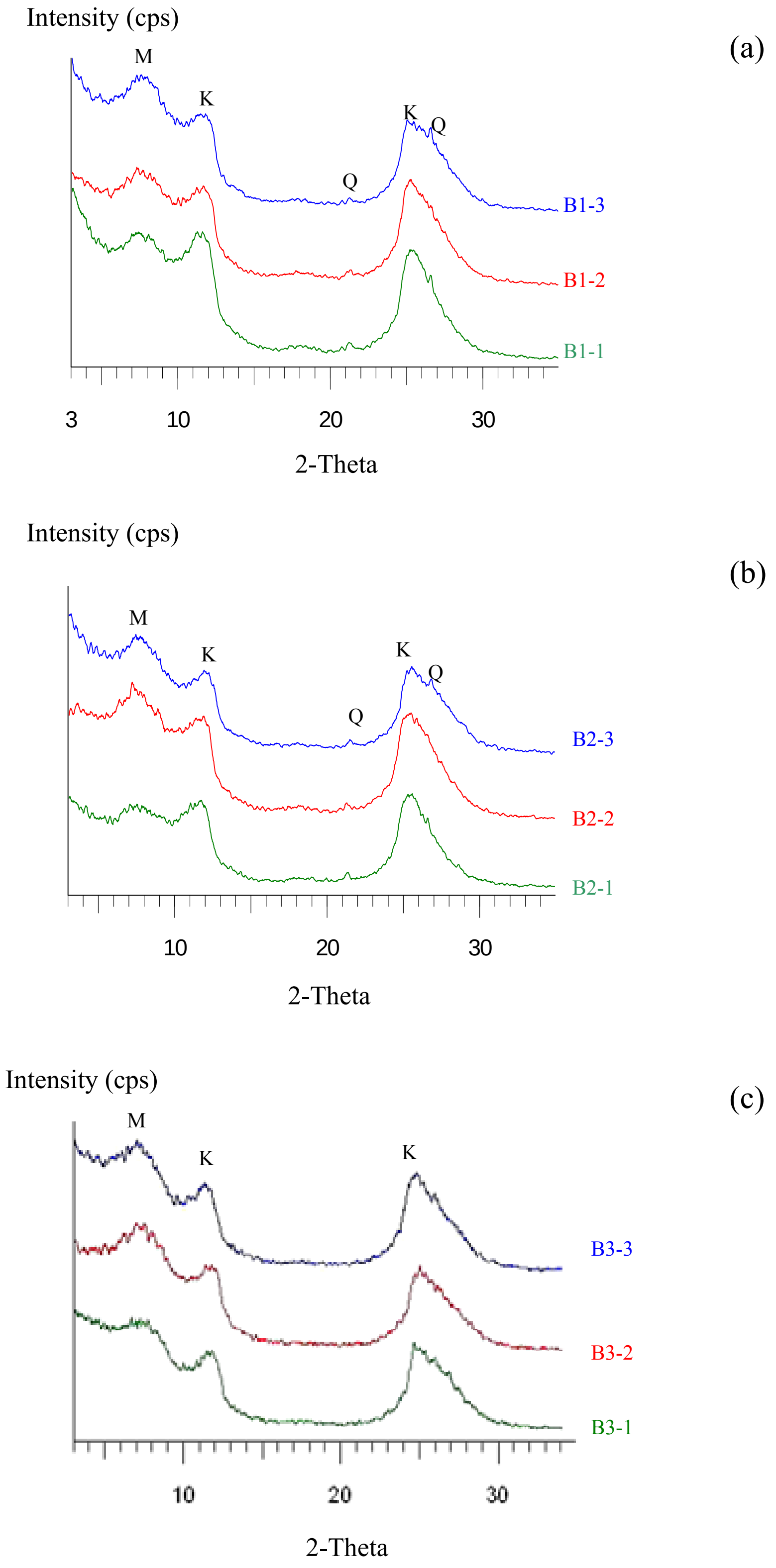


Figure 4.4 XRD patterns of the Na-clay samples at three different depths; (a) sample B1, (b) sample B2 and (c) sample B3. (M: Montmorillonite, K: Kaolinite, Q: Quartz)

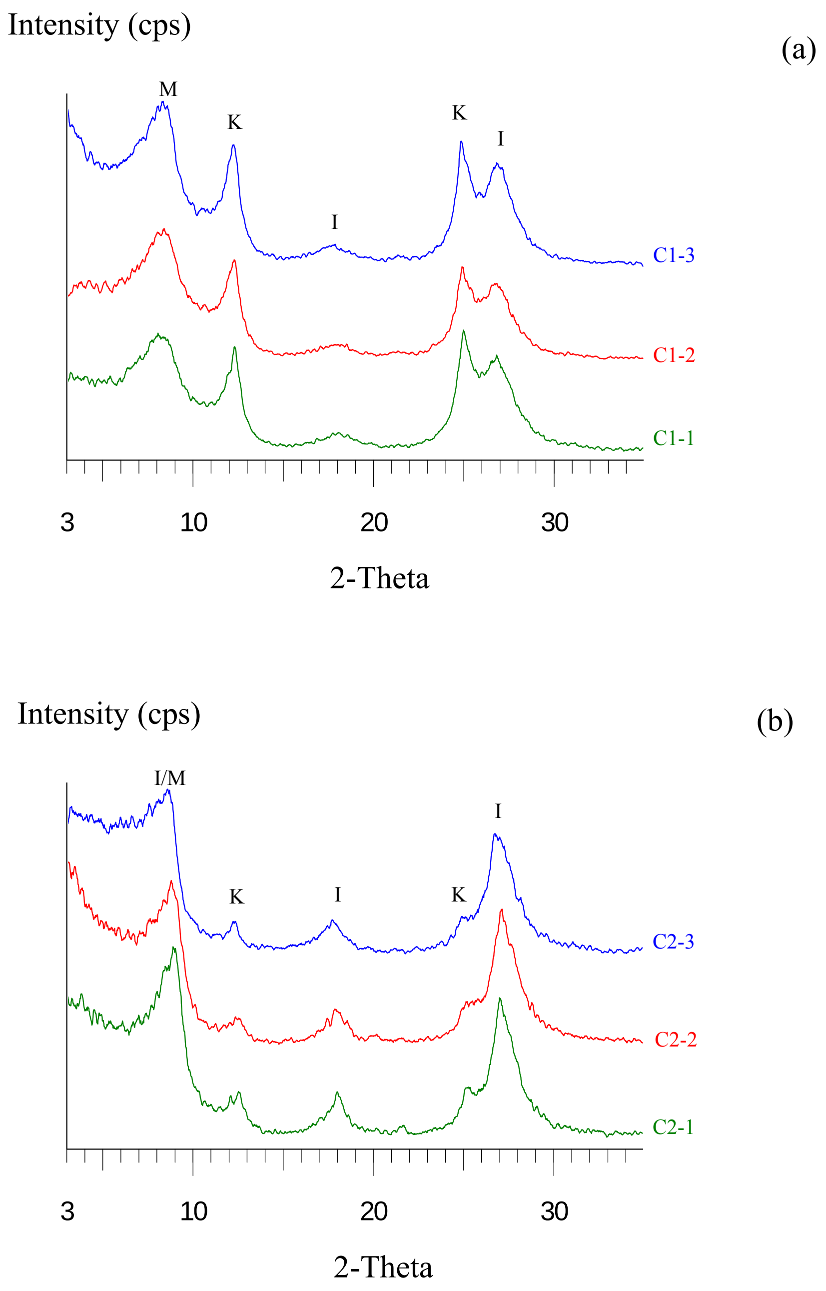


Figure 4.5 XRD patterns of the Na-clay samples at three different depths; (a) sample C1 and (b) sample C2. (M: Montmorillonite, K: Kaolinite, I: Illite, Q: Quartz, I/M: Illite-montmorillonite mixed layer clay)

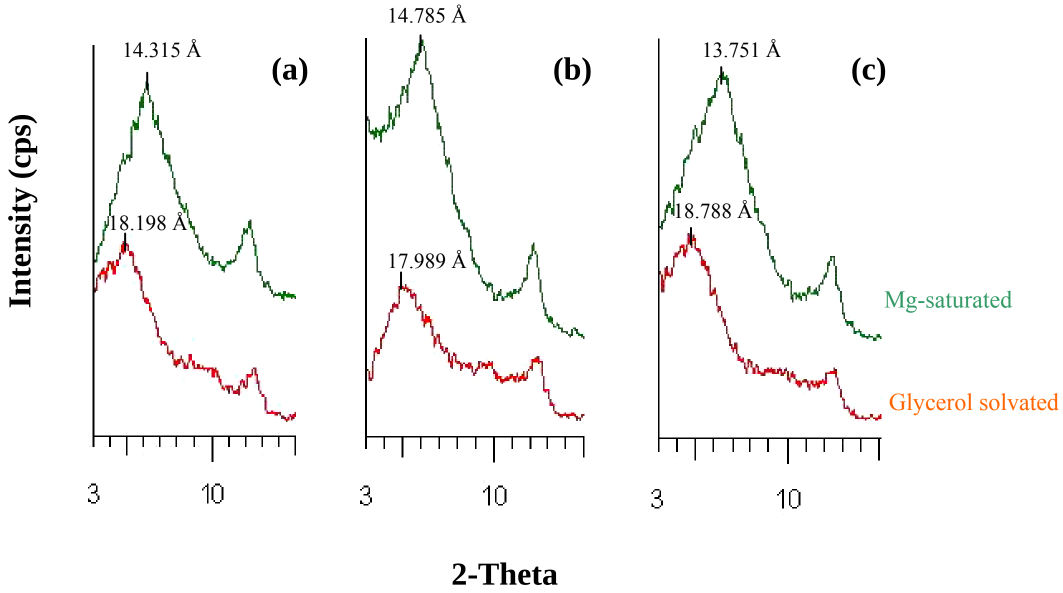


Figure 4.6 XRD patterns of Mg-saturated clay and glycerol solvated clay from Muang District, site 1; (a) sample A1-1, (b) sample A1-2 and (c) sample A1-3.

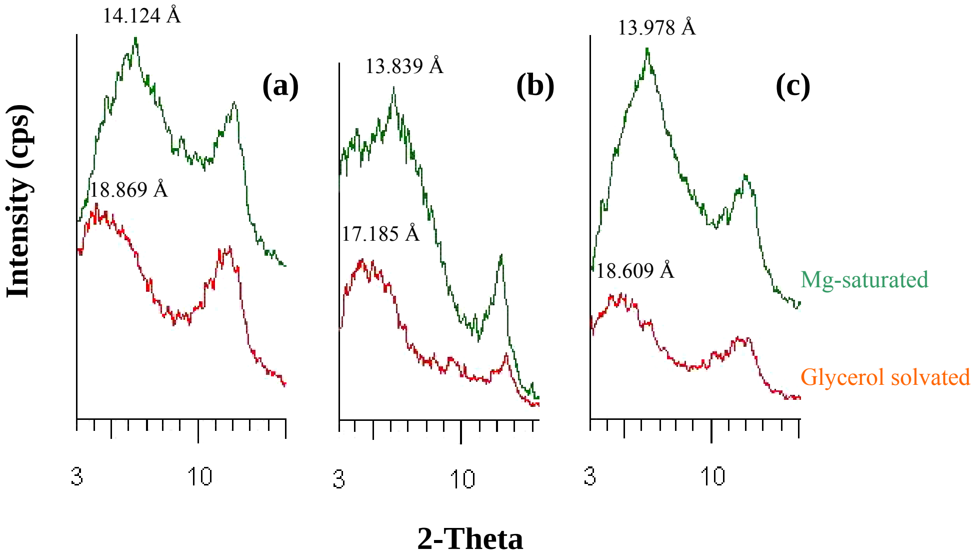


Figure 4.7 XRD patterns of Mg-saturated clay and glycerol solvated clay from Pimai District, site 1; (a) sample B1-1,(b) sample B1-2 and (c) sample B1-3.

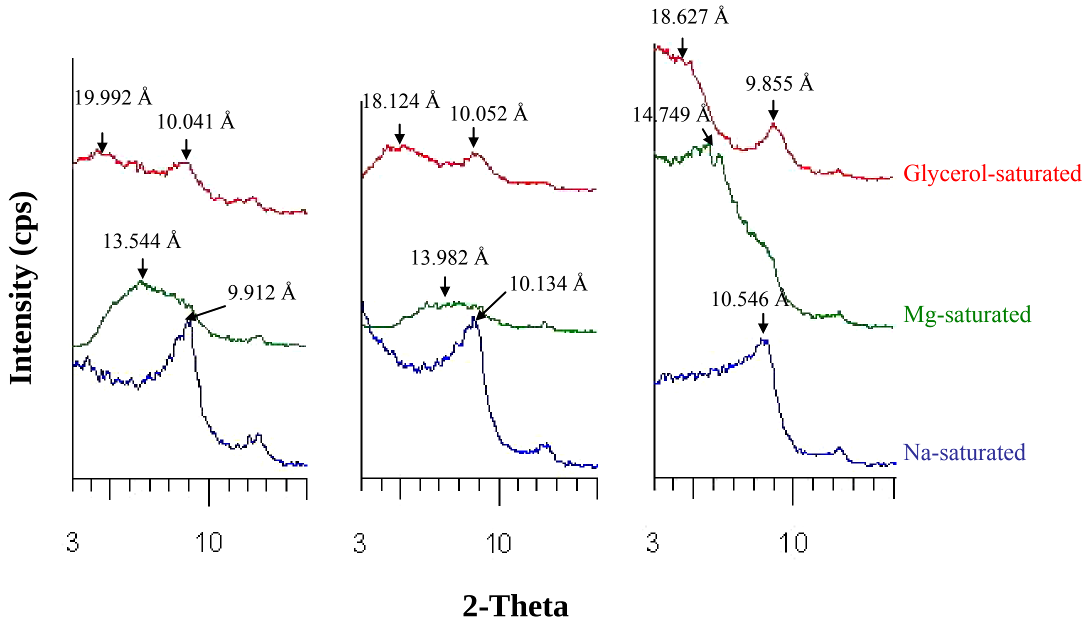


Figure 4.8 XRD patterns of Na-saturated clay, Mg-saturated clay and glycerol solvated clay from Chokchai District, site 2; (a) sample C2-1, (b) sample C2-2 and (c) sample C2-3.

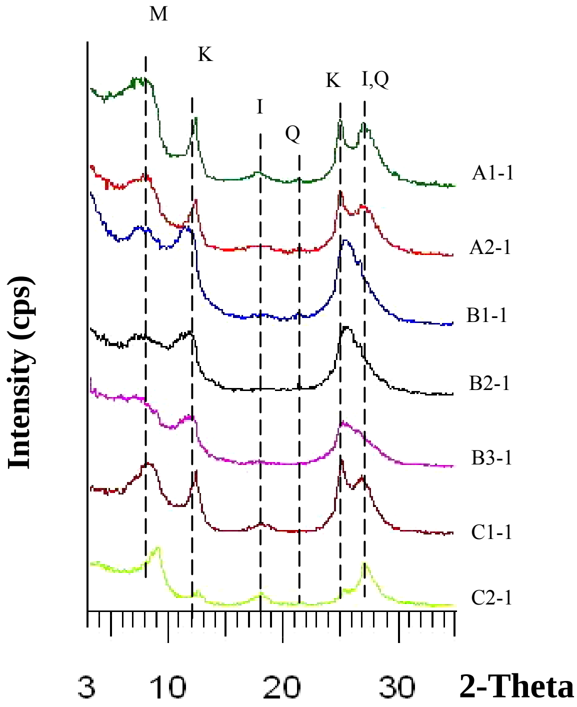


Figure 4.9 XRD patterns of the Na-clay samples at 0-30 cm depth.

Table 4.4 Identification of clay minerals in fine clay fraction of soil samples by X-ray diffraction analysis.

Location (District)	Site	Sample	Depth (cm)	Clay minerals identified			
Muang	1	A1-1	0-30	M	K	I	Q
		A1-2	30-70	M	K	I	Q
		A1-3	70-100	M	K	I	Q
	2	A2-1	0-30	M	K	I	Q
		A2-2	30-70	M	K	I	Q
		A2-3	70-100	M	K	I	Q
Pimai	1	B1-1	0-30	M	K	-	Q
		B1-2	30-70	M	K	-	Q
		B1-3	70-100	M	K	-	Q
	2	B2-1	0-30	M	K	-	Q
		B2-2	30-70	M	K	-	Q
		B2-3	70-100	M	K	-	Q
	3	B3-1	0-30	M	K	-	-
		B3-2	30-70	M	K	-	-
		B3-3	70-100	M	K	-	-
Chokchai	1	C1-1	0-30	M	K	I	-
		C1-2	30-70	M	K	I	-
		C1-3	70-100	M	K	I	-
	2	C2-1	0-30	I/M	K	I	-
		C2-2	30-70	I/M	K	I	-
		C2-3	70-100	I/M	K	I	-

M: Montmorillonite, I/M: Illite-montmorillonite mixed layer clay**,** K: Kaolinite, I: Illite, Q: Quartz

A semiquantitative XRD analysis was done using a DIFFRAC plus computer program; a software within the X-ray diffraction spectrometer, D5005 X-ray, Bruker. The program allows one to calculate the major diffraction peak heights. The program requires the measurements the left and right angles (2-Theta) of the peaks. The measuring of net height, raw area and finally the net area are followed. The net area of peaks are converted to the percentages (Department of Geology, Institute of Geosciences and Astronomy, Oulu University, www, 2002). Table 4.5 demonstrates how the program works by using sample A1-1 as an example. There were four peaks of montmorillonite, kaolinite, illite and quartz in the sample diffractogram (Figure 4.10). The peak areas calculated for these peaks were 466, 130, 44 and 5 respectively. The total net area was 645, and thus individual mineral percentages are calculated as 72%, 20%, 7% and 1% respectively, as compared to the total net area. The results obtained from 21 clay samples are shown in Table 4.6.

Table 4.5 Semiquantitative XRD analysis of sample A1-1.

Sample	Left Angle	Right Angle	Net height	Raw Area	Net Area	%
	2-Theta	2-Theta	Cps	Cps x2-Theta	Cps x2-Theta	mineral
A1-1	3.90	10.20	149	1668	466	72% M
	10.34	13.94	138	379	130	20% K
	15.54	19.30	25	152	44	7% I
	20.12	22.12	14	54	5	1% Q

M: Montmorillonite, K: Kaolinite, I: Illite, Q: Quartz

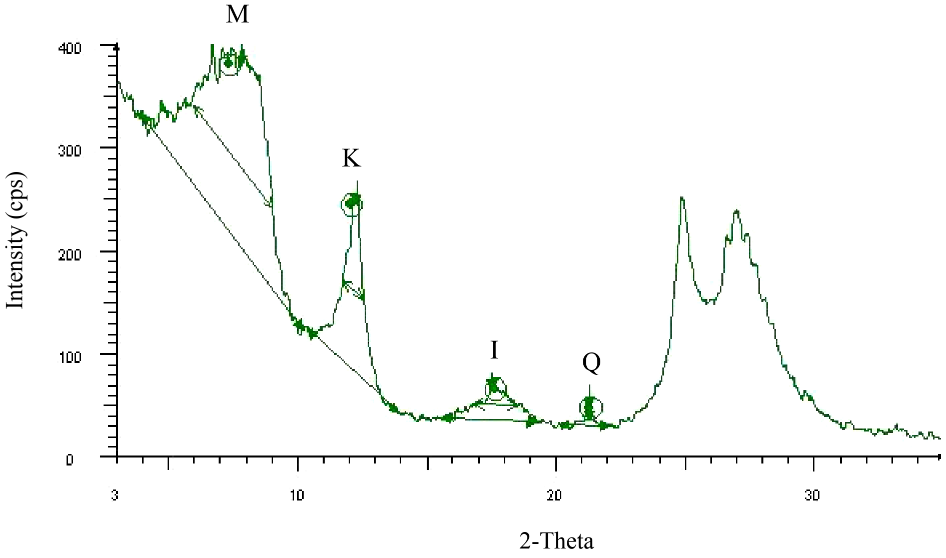


Figure 4.10 XRD pattern of sample A1-1.

Table 4.6 Relative clay minerals abundance in the separated fine clay fraction of soil samples.

Location (District)	Site	Sample	Depth (cm)	M (%)	I/M (%)	K (%)	I (%)	Q (%)
Muang	1	A1-1	0-30	70	-	21	8	1
		A1-2	30-70	76	-	18	6	<1
		A1-3	70-100	75	-	20	5	<1
	2	A2-1	0-30	63	-	29	6	2
		A2-2	30-70	61	-	28	9	2
		A2-3	70-100	64	-	27	7	2
Pimai	1	B1-1	0-30	33	-	67	-	<1
		B1-2	30-70	49	-	51	-	<1
		B1-3	70-100	55	-	45	-	<1
	2	B2-1	0-30	32	-	68	-	<1
		B2-2	30-70	55	-	45	-	<1
		B2-3	70-100	59	-	41	-	<1
	3	B3-1	0-30	52	-	48	-	-
		B3-2	30-70	65	-	35	-	-
		B3-3	70-100	55	-	45	-	-
Chokchai	1	C1-1	0-30	60	-	30	11	-
		C1-2	30-70	62	-	30	8	-
		C1-3	70-100	63	-	29	8	-
	2	C2-1	0-30	-	77	8	15	-
		C2-2	30-70	-	77	6	17	-
		C2-3	70-100	-	72	6	22	-

M: Montmorillonite, I/M: Illite-montmorillonite mixed layer clay, K: Kaolinite, I: Illite, Q: Quartz

4.4.2 Infrared analysis

All the Na-clay samples exhibit bands associated to montmorillonite, kaolinite, illite and quartz. The most distinguish feature of the montmorillonite spectrum is the broad absorption band that ranges from 3,300-3,500 cm^{-1} (Figures 4.11-4.12). The band at 3,459 cm^{-1} is due to H-O-H stretching of water molecules in the interlayer region of montmorillonite. Other prominent bands in the montmorillonite spectrum include a very broad O-H stretching band at 3,622 cm^{-1} and OH deformation band at 912 cm^{-1} (AlAlOH). The broad O-H stretching band at 3,622 cm^{-1}, is the overall envelope for a wide range of AlAlOH and AlMgOH environments in the highly substituted and distorted structure. This band occurs close to that of the inner OH groups in kaolinite (Russell and Fraser, 1994). The band at 1,638 cm^{-1} corresponds to OH bending vibration (Bala et al., 2000).

Kaolinite shows a characteristic IR absorption in the 3,600-3,700 cm^{-1} region. These absorbance correspond to the stretching vibrations of the inner surface Al-OH at 3,699 cm^{-1} and the inner Al-OH at 3,622 cm^{-1}. Absorbance at 695 cm^{-1} and 533 cm^{-1} are due to Si-O deformation of kaolinite (Olson, Thompson and Wilson, 2000).

Infrared features of illite are rarely diagnostic because illite is so variable in the chemical composition. The broad O-H stretching band near 3,625 cm^{-1}, ranging down below 3,620 cm^{-1} in some instances, coupled with the 825 cm^{-1} (Al-Mg-OH), 750 cm^{-1} (Al-O-Si) doublet is almost certainly diagnostic (Russell, 1987).

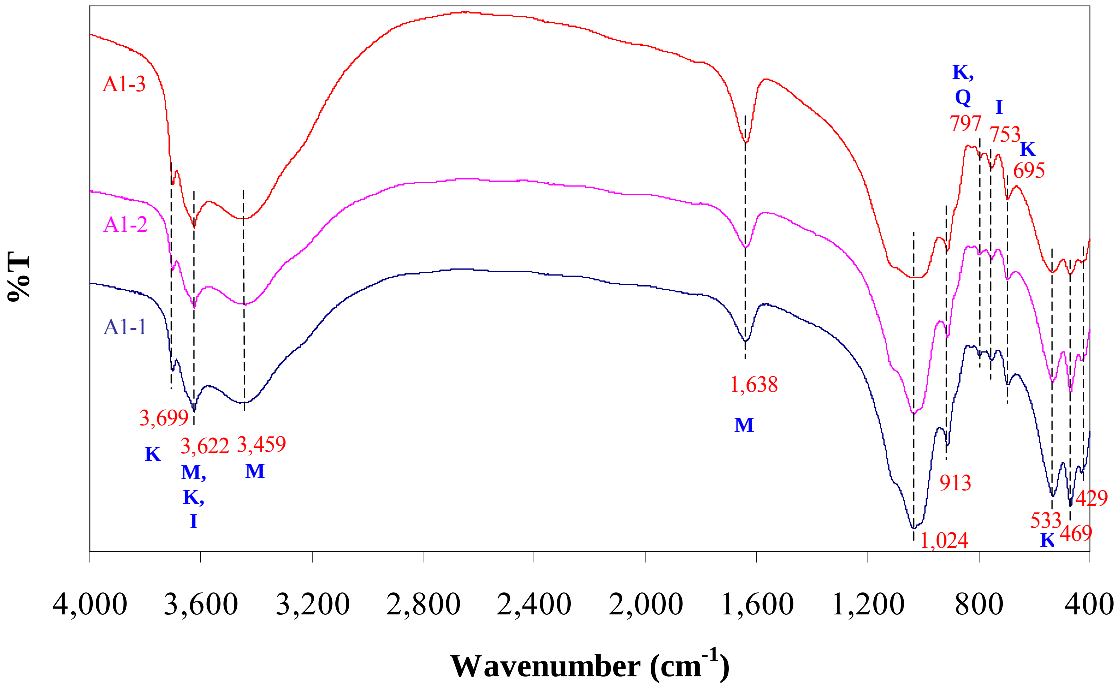


Figure 4.11 FTIR spectra of the Na-clay samples from Muang District, site 1

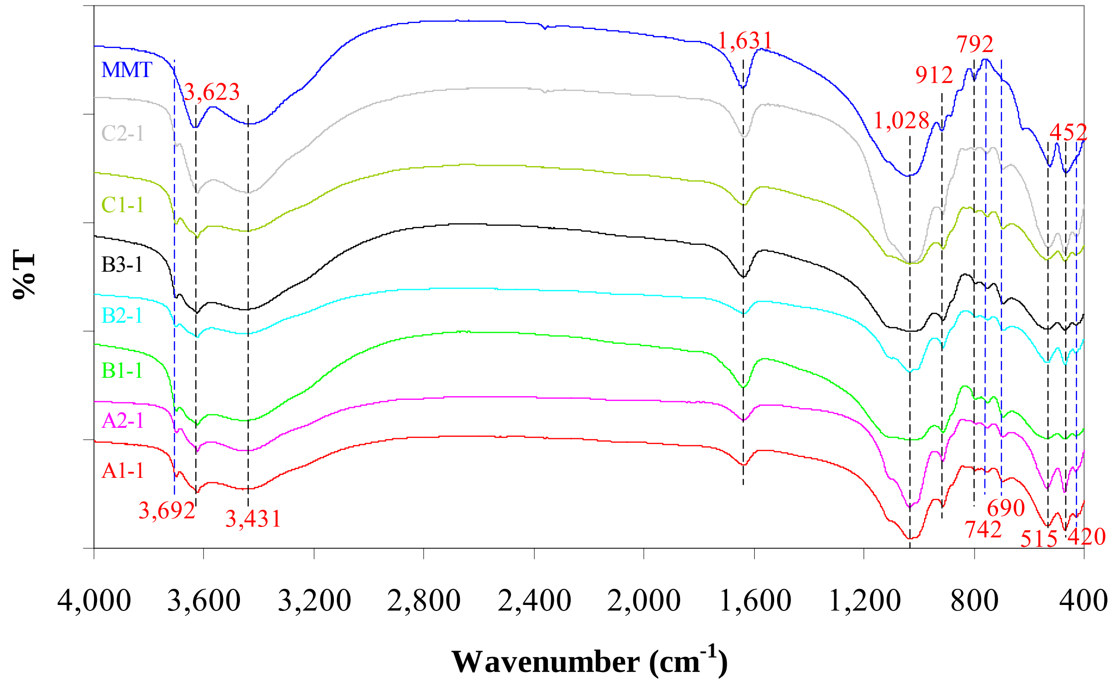


Figure 4.12 FTIR spectra of the Na-clay samples from seven sites.

4.4.3 Thermal analysis

Figure 4.13 shows the TGA and DTG curves of the Na-clay sample. The removal of absorbed and adsorbed water molecules residing between montmorillonite crystalline occurs at about 100°C. The interlayer water molecules residing between the aluminosilicate layers and comprising the hydration spheres of the cations evolve at about 300°C. The weight loss in the temperature range 400-1000°C may due to the dehydroxylation of the aluminosilicate lattice.

The differential thermal analysis of the Na-clay sample (Figure 4.14) shows an intense endothermic peak at 99.94°C. This peak can be due to loss of water molecules absorbed and adsorbed in the interlayer or coordinated with exchangeable cations. The characteristic peak observed at about 500°C is due to loss of structural hydroxyl groups in iron rich smectite. This peak is quite different from the usual 700°C endothermic peak of montmorillonite from the Clays Repository, Wyoming, USA. (Figure 4.15). The decrease of the temperature of the endothermic reaction to 550-600°C could be caused by a large replacement of Al by Fe in octahedral position (Kishk et al., 1976). The crystalline structure of the smectite is preserved after the loss of the hydroxyl groups until 800°C. Above 800°C, double peaks, endo-exothermic, appear at 909°C and 931°C, respectively. The endothermic peaks represent the destruction of the crystalline framework, while the exothermic peaks represent the formation of α or β mulite quartz (Guarino et al., 1997; Paterson and Swaffield, 1987).

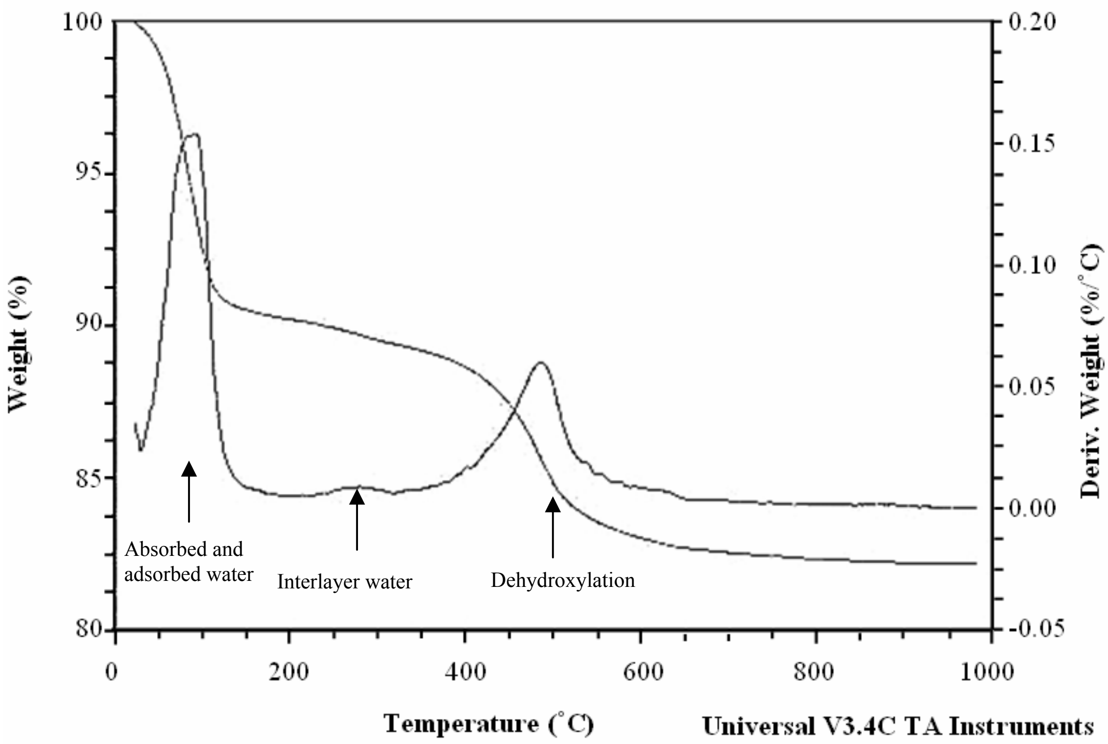


Figure 4.13 TGA and DTG curves of Na-clay sample.

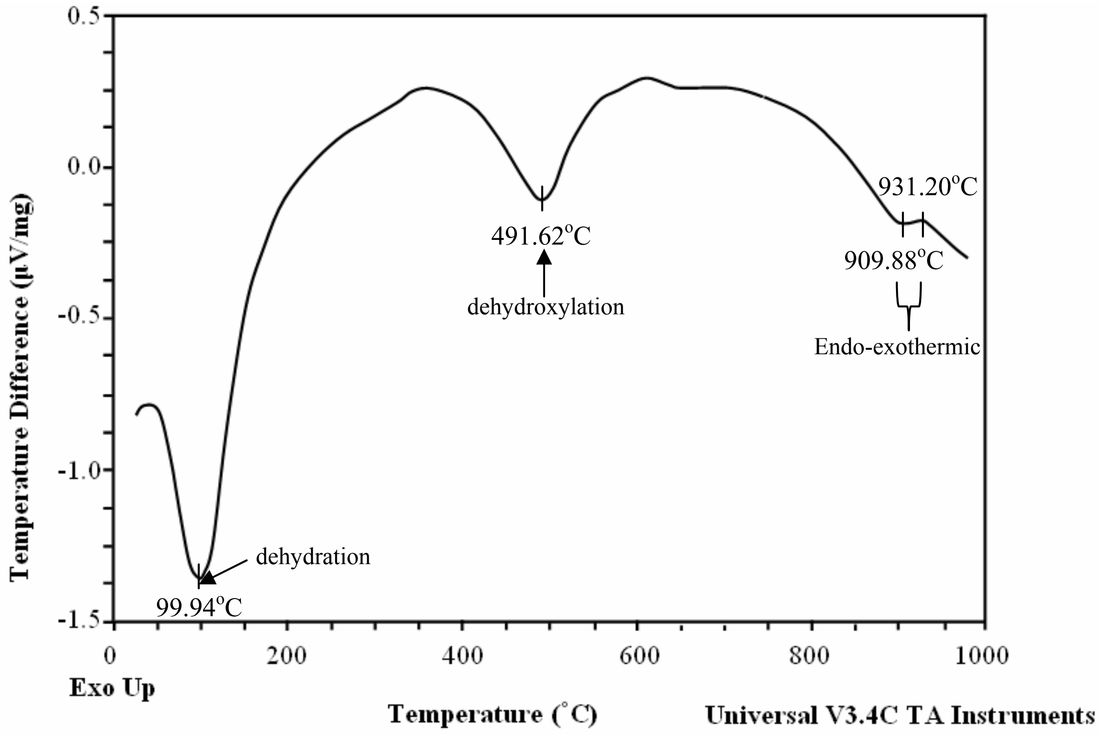


Figure 4.14 DTA curve of Na-clay sample.

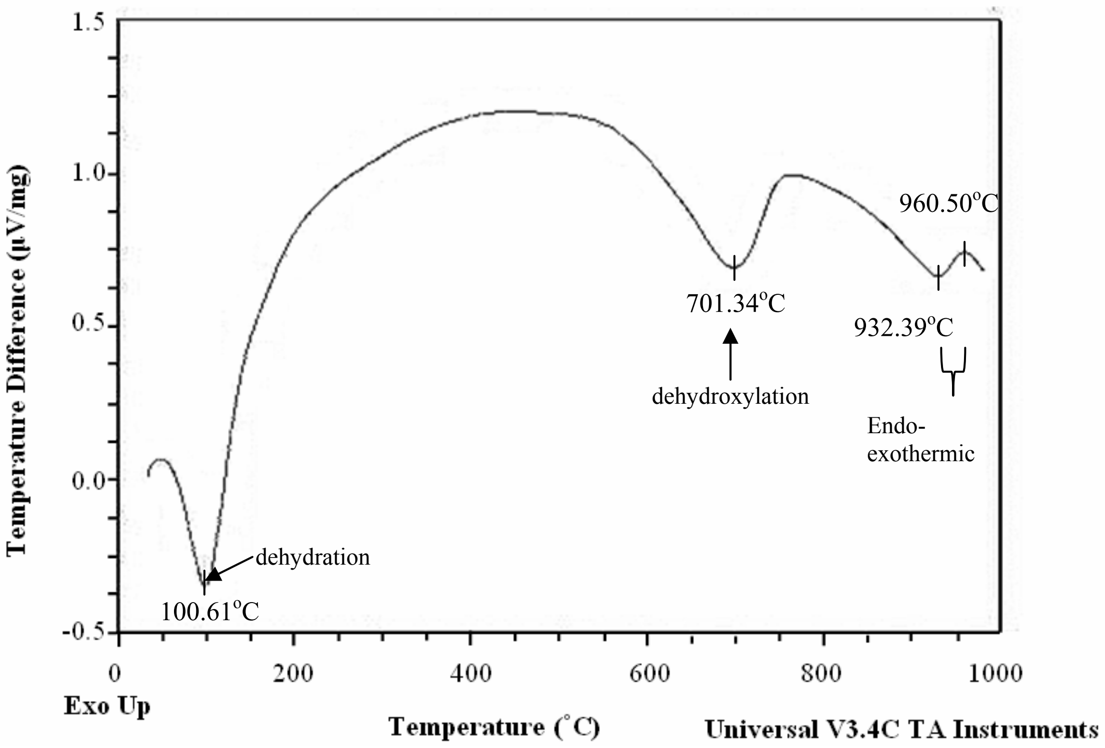
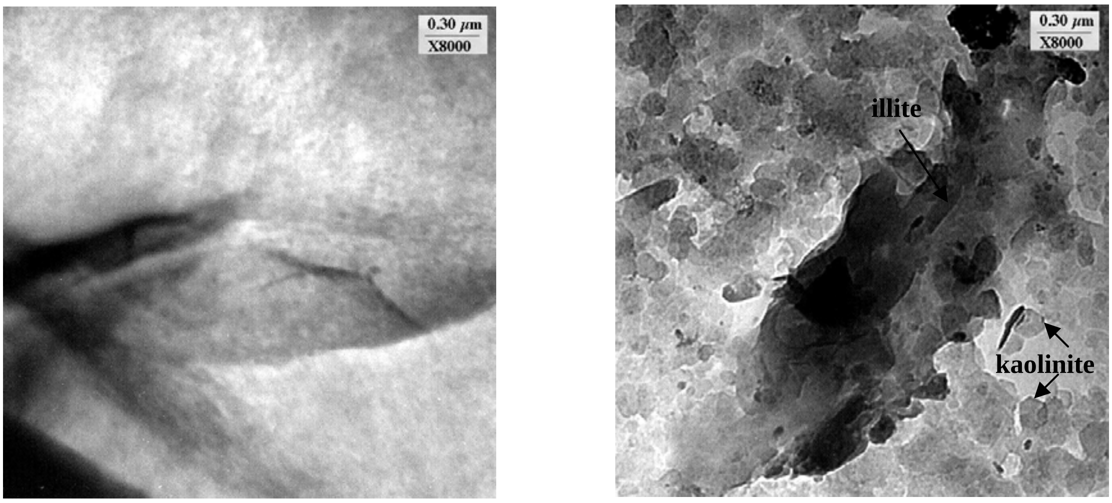


Figure 4.15 DTA curve of montmorillonite (SWy-2) obtained from the Clays Repository, Wyoming, USA.

4.4.4 Transmission electron microscope

The TEM micrographs of the Na-clay samples (Figure 4.16 (a), (b)) present typical aspects of clay minerals from the smectite group, with irregular profile particles, undefined shape and great tendency to present curled edges, probably due to the small plate diameter. Some irregular flake-shaped aggregates can be seen due to the attraction between the particles. The hexagonal profile and lath-shaped of the particles can be observed in Figure. 4.16(b), indicating the presence of kaolinite and illite, respectively, which are confirmed by X-ray results. Figure 4.17 shows the TEM micrograph of commercial montmorillonite (SWy-2), irregular fluffy masses of extremely small particles can be observed (Grim, 1953; Nadeau and Tait, 1987).



(a) (b)

Figure 4.16 TEM Micrographs of the Na-clay samples.

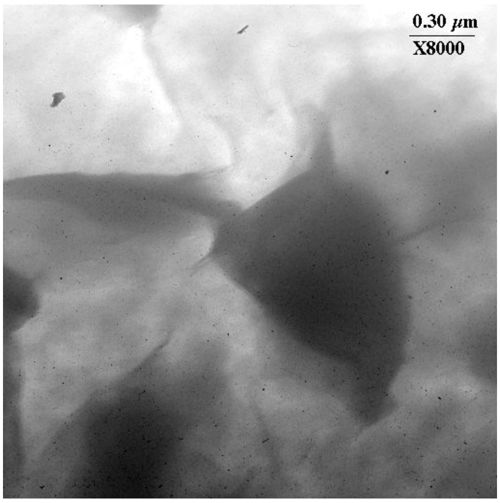


Figure 4.17 TEM Micrograph of commercial montmorillonite (SWy-2).

4.4.5 Scanning electron microscope

Scanning electron microscopy imaging is used as a supplemental analysis. Since identification via SEM can be ambiguous at the clay size and quantified only subjective. SEM images are only used to support the information derived from XRD, TGA, DTA, TEM and FTIR. Images of commercial montmorillonite (SWy-2), sample A2-1 and sample B1-1 are taken for the illustrations in Figure 4.18. Divided platy forms with poorly defined shapes and very crumpled layers can be seen (McHardy and Birnie, 1987).

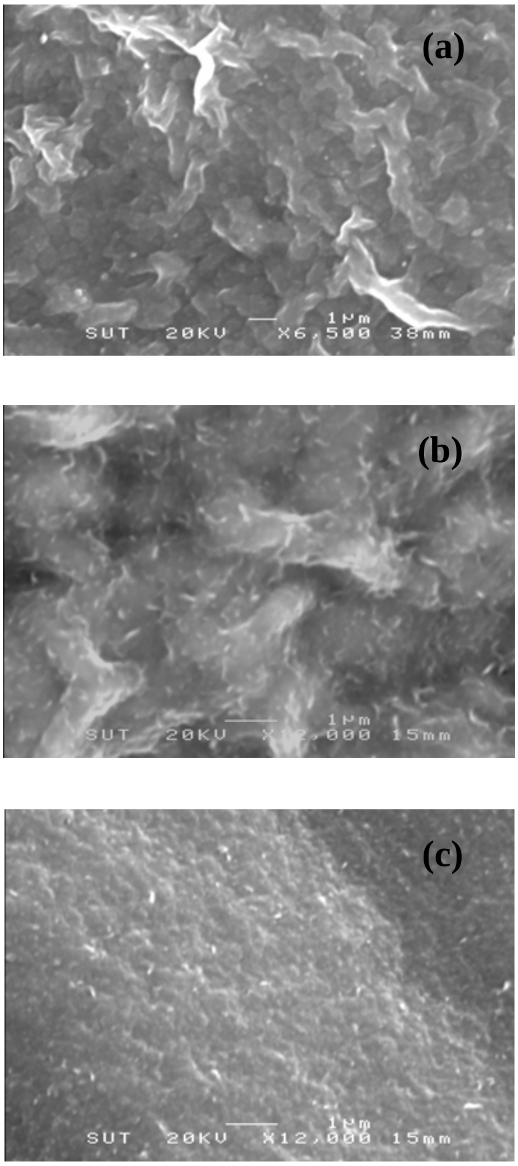


Figure 4.18 SEM micrographs; (a) commercial montmorillonite (SWy-2), (b) sample A2-1 and (c) sample B1-1.

4.5 Characterization of modified montmorillonite

4.5.1 X-ray diffraction

The hydrophilic surface layers of both Na-clay sample and Na-montmorillonite (SWy-2) were modified by dispersing montmorillonite uniformly into organic modifier solution (1-hexadecylamine; $C_{16}H_{35}N$). The alkylammonium ions with chain length larger than eight carbon atoms were favouring the synthesis of delaminated nanocomposites (Lan et al., 1995). This organically modified montmorillonite will be further studied by the research group of Assistant Professor Dr. Visit Vao-soongnern, the School of Chemistry, Suranaree University of Technology.

The properties of organoclays are investigated by basal X-ray diffraction analysis. The basal spacings (001 diffraction peak) of the original Na-clay sample changes from 11.896 Å to 22.803 Å after modification. While the d-spacing of commercial montmorillonite (SWy-2) changes from 14.214 Å to 17.850 Å. The organoclay displays a greater interlayer spacing than the corresponding unmodified clay (Figures 4.19-4.20). The increase of interlayer spacing is due to the intercalation of the organic modifier solution into the interlayer of structure. When the hydrated cations (sodium ions) are ion-exchanged with organic cations, the organoclay becomes organophillic. Its surface energy is lower and is more compatible with organic polymers. These polymers may be able to intercalate within the galleries. These organoclay can be used in the synthesis of nanocomposites.

Figure 4.19 shows the comparison of XRD patterns between the unmodified Na-clay sample and the organically modified clay sample. The settings of XRD experiments were not the same since the unmodified sample was prepared using aqueous suspension of clay on glass slide (preferentially oriented) while the modified sample was prepared using the Polymethyl metaacrylate (PMMA) sample holder (randomly oriented). Since the interlayer distance of the modified clay increased from 11.896 Å (unmodified) to 22.803 Å, the slit settings were also different. The unmodified sample slit settings were: 0.1° divergence slit, 0.1° anti-scatter slit and 0.6 mm receiving slit while the slit settings of the modified sample were: 1.0° divergence slit, 1.0° anti-scatter slit and 0.2 mm receiving slit. So it was necessary to scan from 3° 2θ for unmodified sample and from 1° 2θ for the modified sample. The explanations were also applicable for Figure 4.20 of commercial montmorillonite.

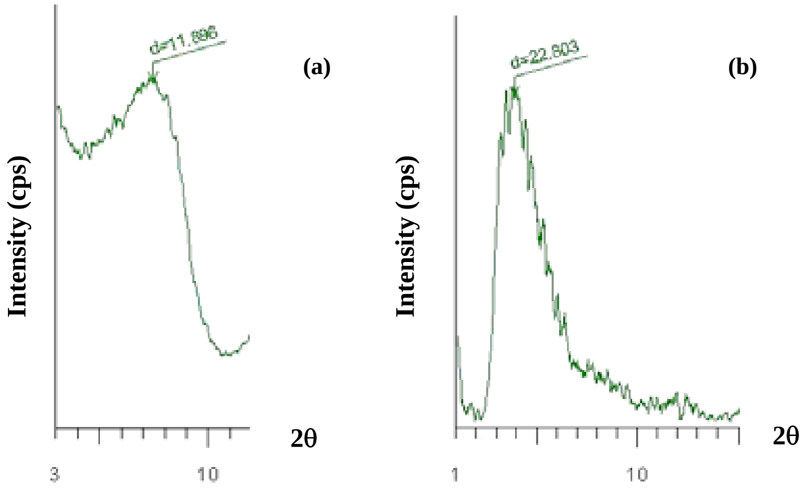


Figure 4.19 X-ray diffraction patterns of sample A1-1; (a) unmodified, preferentially oriented Na-clay sample (b) organically modified randomly oriented sample.

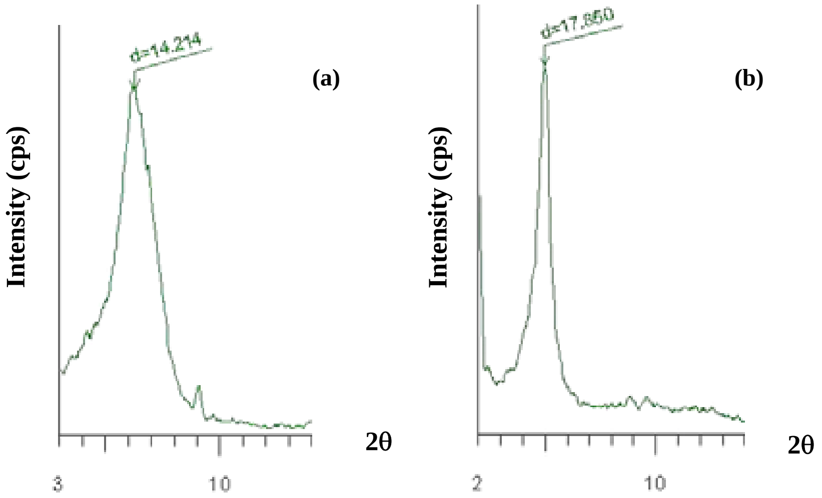


Figure 4.20 X-ray diffraction patterns of commercial Na-montmorillonite (SWy-2); (a) before modification, preferentially oriented sample (b) after organically modification, randomly oriented sample.

4.5.2 Thermogravimetric analysis

For TGA analysis, the thermal decomposition expressed in term of weight loss as a function of temperature for the organically modified clay sample is graphically shown in Figure 4.21. The TGA and DTG curves are considered in four temperature ranges; (1) loss of absorbed and adsorbed water at the temperature below 200°C, (2) evolution of organic substance at the temperature ranges 200-550°C, (3) loss of the structural water at the temperature ranges 550-800°C and (4) the temperature ranges between 800-1000°C where organic carbon reacts in some yet unknown way (Xie, Liu et al., 2001; Xie, Pan et al., 2001). Figure 4.22 shows TGA and DTG curves of organically modified commercial montmorillonite (SWy-2). Thermal decomposition can be considered at four temperature ranges the same as the organically modified clay sample.

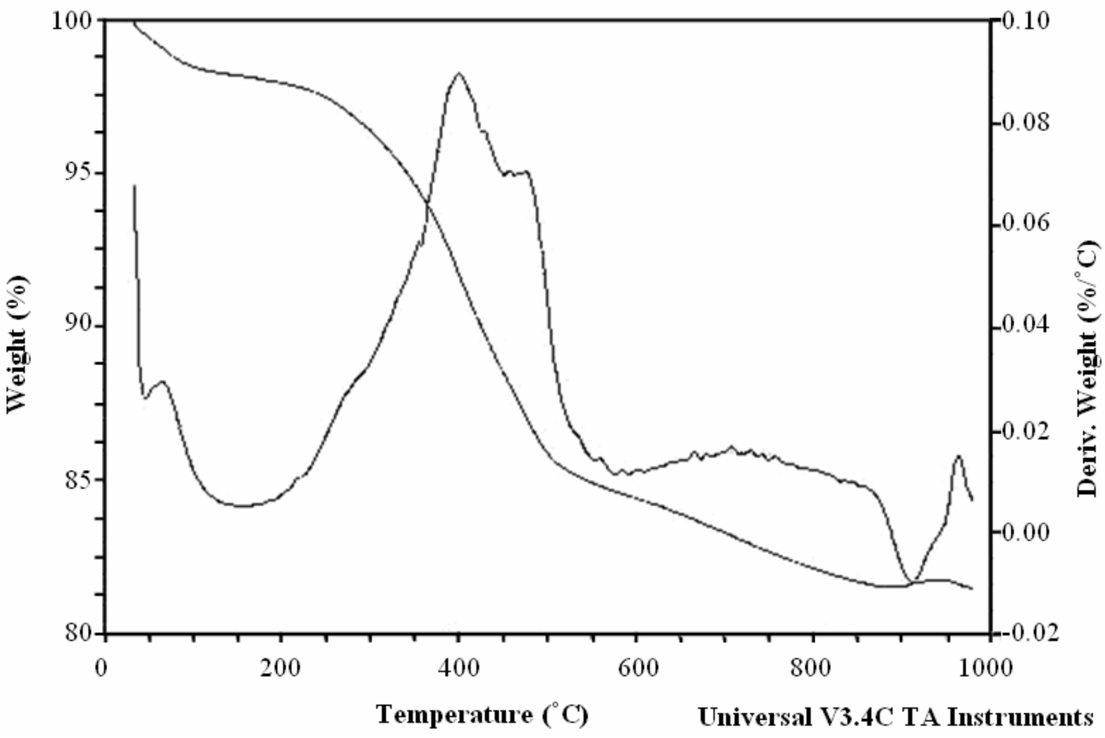


Figure 4.21 DTG and TGA curves of organically modified clay sample.

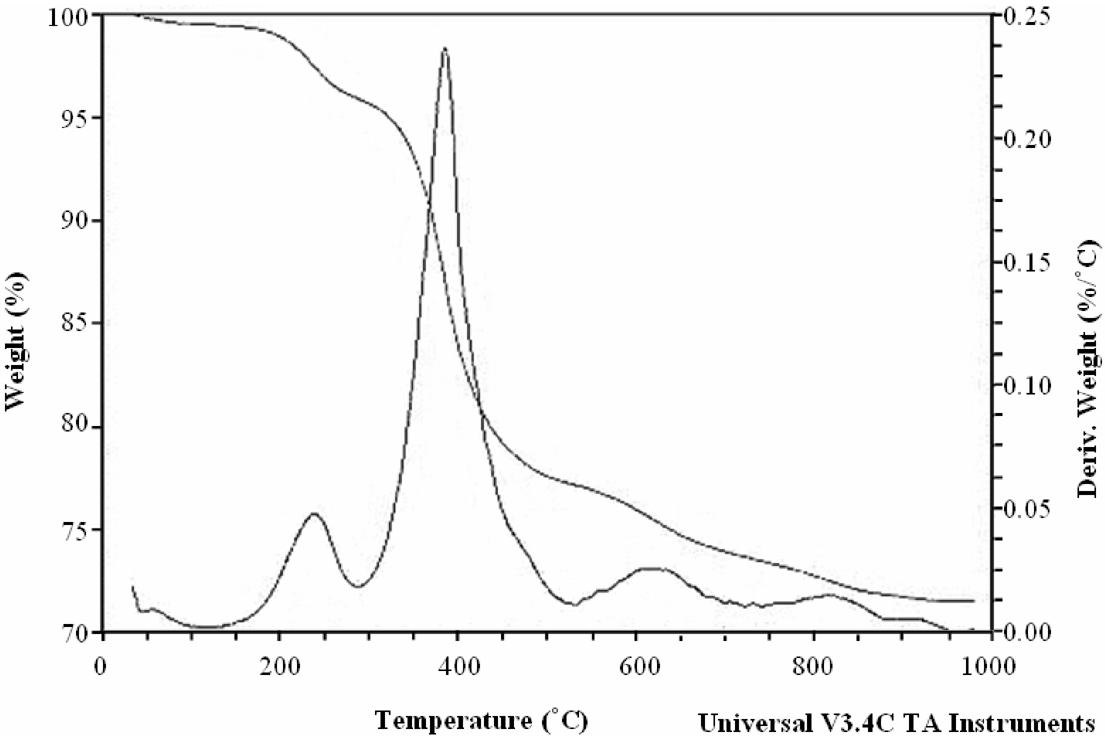


Figure 4.22 DTG and TGA curves of organically modified commercial montmorillonite (SWy-2).

4.5.3 Infrared analysis

Figure 4.23 illustrates the FTIR results of the unmodified Na-clay sample and the organically modified clay. The common features in these spectra are the presence of bands at 3,622 cm^{-1}, 3459 cm^{-1} and 1631 cm^{-1} originate from the OH (free), OH (hydrogen bond) and OH (bending). The spectrum of organically modified clay sample shows the presence of three new bands at 2,918 cm^{-1}, 2,850 cm^{-1} and 1,466 cm^{-1}, which are due to C-H asymmetric stretching vibrations of intercalated primary aliphatic ammonium, the symmetrical C-H stretching absorption band and the -CH$_2$- scissor vibrational band, respectively (Vaia, Teukolsky and Giannelis, 1994; Bala, Samantaray and Srivastava, 2000; Arroyo, López-Manchado and Herrero, 2003).

Figure 4.24 shows FTIR spectra of organically modified commercial montmorillonite (SWy-2) and organically modified clay sample. Each spectrum shows the three new peaks. The absorption bands occur at the same wavenumbers (cm^{-1}).

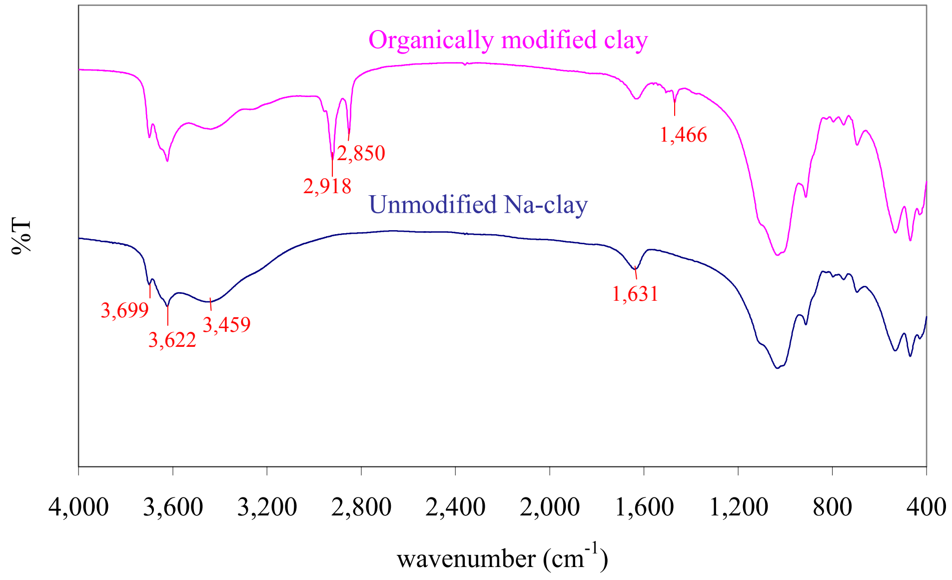


Figure 4.23 FTIR spectra of unmodified Na-clay and organically modified clay.

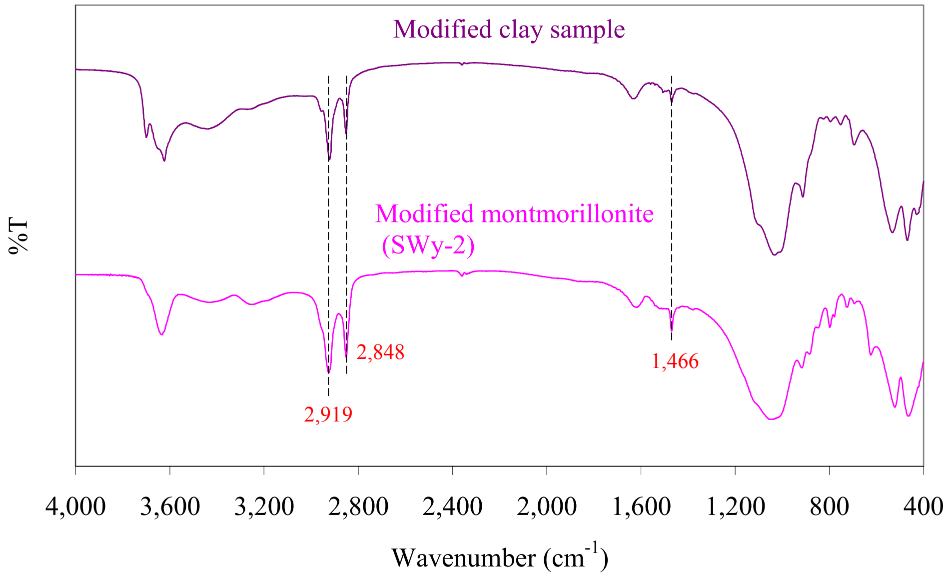


Figure 4.24 FTIR spectra of organically modified montmorillonite (SWy-2) and organically modified clay sample obtained from the separation.

CHAPTER V

CONCLUSIONS

The separation, characterization and modification of montmorillonite in clay from Nakhonrationsima Province were carried out in this thesis.

The technique of dispersion in water after removal of carbonates and organic matter were used to separate clay particles from vertisol soil. The 0.2 μm clay fractions were separated by centrifugation method. The sample obtained is prepared in the form of sodium saturated clay. The original soil samples contained about 28-68% by weight Na-clay.

The predominant clay mineral in the Na-clay was montmorillonite. The abundant of montmorillonite was higher than 60% in Ban Tanlon, Ban Natom, Tambol Muenwai, Muang District and Ban Bungthapprang, Tambol Chokchai, Chokchai District. Other clay minerals such as kaolinite, illite and illite-montmorillonite (I/M) mixed layer were also found. Kaolinite was found in all Na-clay sample in moderate amounts, 6-68%. Iillite was found in Na-clay sample from Muang and Chokchai Districts in minor amounts, 5-22%. Illite-montmorillonite (I/M) mixed layer was found only in Ban Donphlai, Tambol Thayiam, Chokchai District in high abundant, >72%. Quartz was also present in trace amount, ≤ 2%.

As part of the characterization of montmorillonite in clay, XRD was used primarily to identify the clay minerals based on the basal d-spacings under different conditions. XRF, FTIR, SEM, TEM and thermal analysis (TGA and DTA) were used as complementary to the main investigation technique. Most of the results from the studies were comparable with the results obtained from commercial Na-montmorillonite (SWy-2) bought from the Source Clays Repository, Wyoming, USA.

The modification of montmorillonite in the 0.2 μm separated clay was also carried out in this work. Na-clay and Na-montmorillonite (SWy-2) samples were modified by exchanging Na ions with organic cations. The increase in the basal spacing suggested the intercalation of hexadecylamine in the interlayer space. The presence of alkyl ammonium ions in the interlayer space was also confirmed independently by FTIR, and was manifested by the appearance of the bands corresponding to CH_3, CH_2 and CH vibrations. The presence of hexadecylamine in the interlamellar space had been confirmed by TGA. Decomposition of the intercalating agents had occurred in the range 200-550°C.

In summary, this work was carried out to separate montmorillonite in clay and to modify the separated montmorillonite. The separated montmorillonite is not in the pure form but contains higher percentages of montmorillonite. The potential applications of the separated montmorillonite and modified montmorillonite will be the future work of those who are interested. Especially, the synthesis of polymer clay nanocomposite which will used these material for the application in nanotechnology.

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APPENDICES

APPENDIX A

MAP OF VERTISOL SOIL DISTRIBUTION IN NAKHONRATCHASIMA PROVINCE

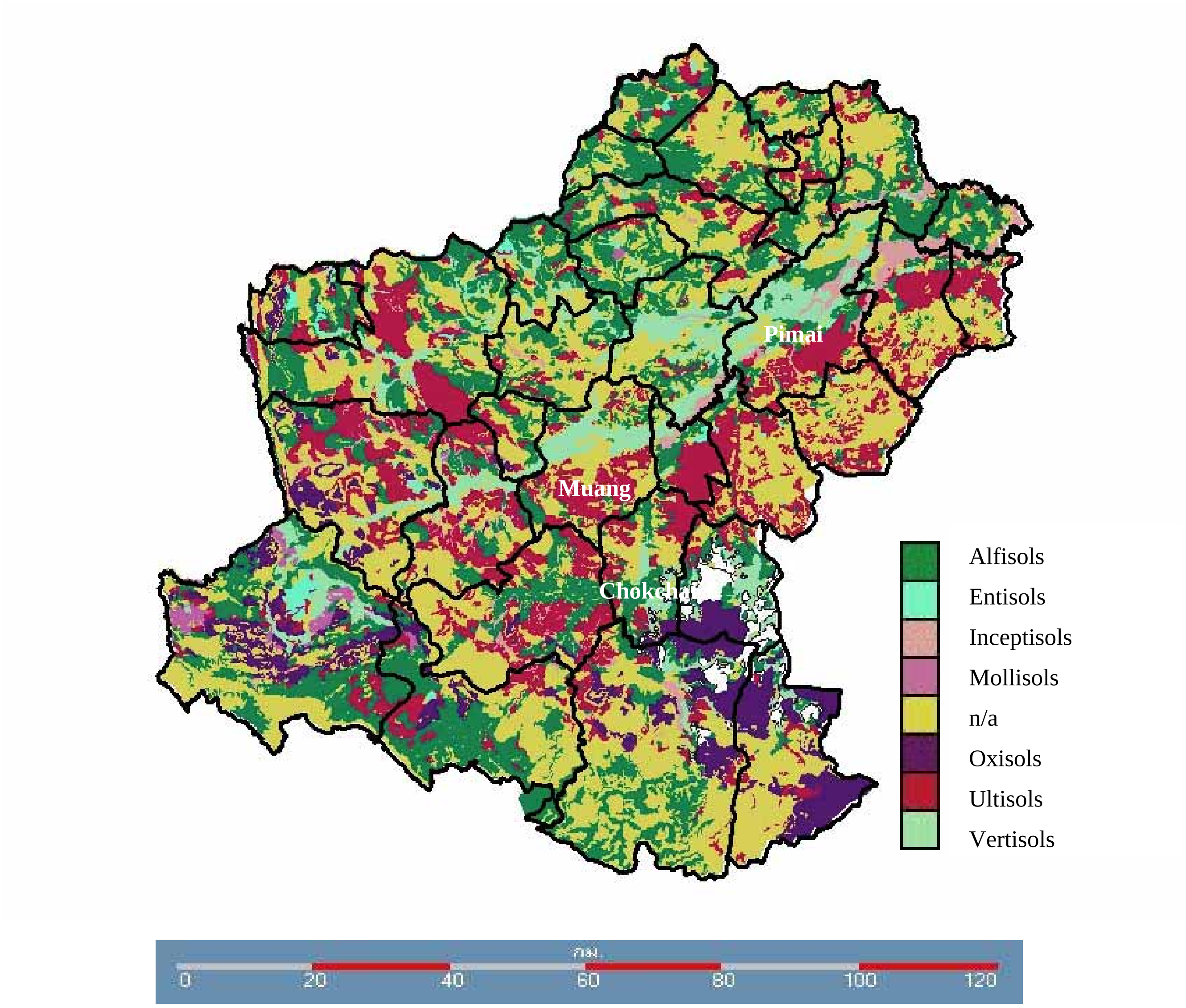

Figure A.1 Map of vertisol soils in Nakhonratchasima Province showing the locations where soil samples were collected; Muang, Pimai and Chok chai districts.

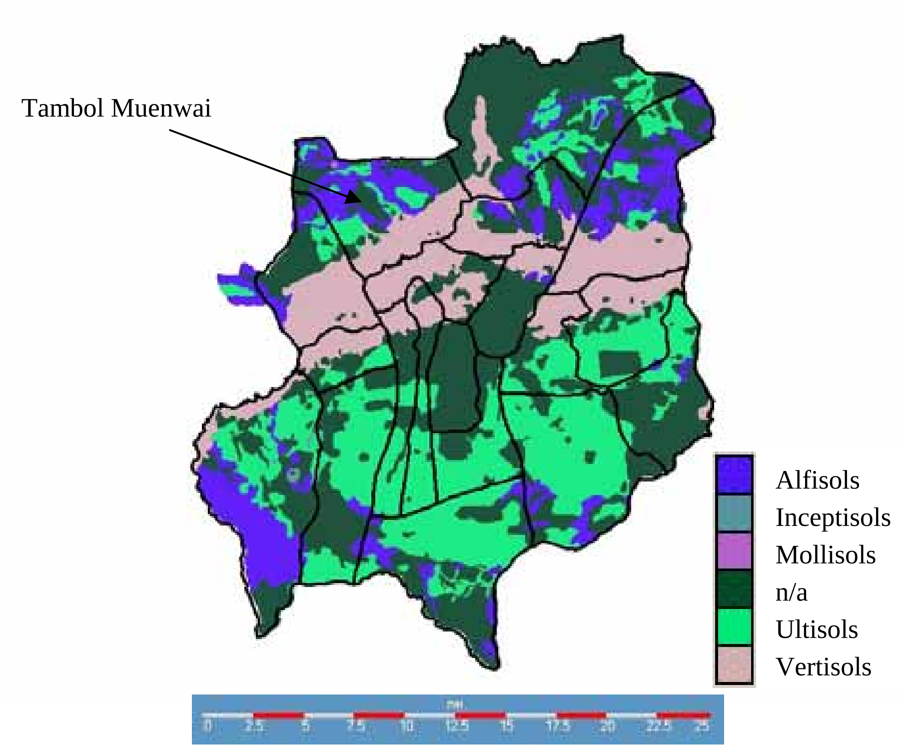

Figure A.2 Map of vertisol soils in Muang district showing the location where soil samples were collected; Tambol Muen Wai.

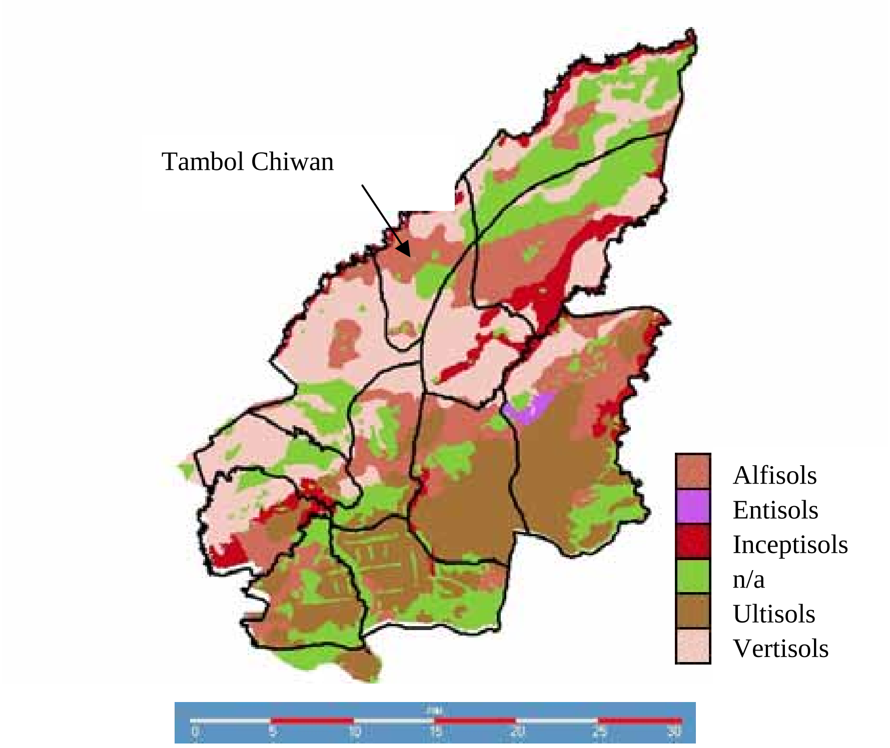

Figure A.3 Map of vertisol soils in Pimai district showing the location where soil samples were collected; Tambol Chi Wan.

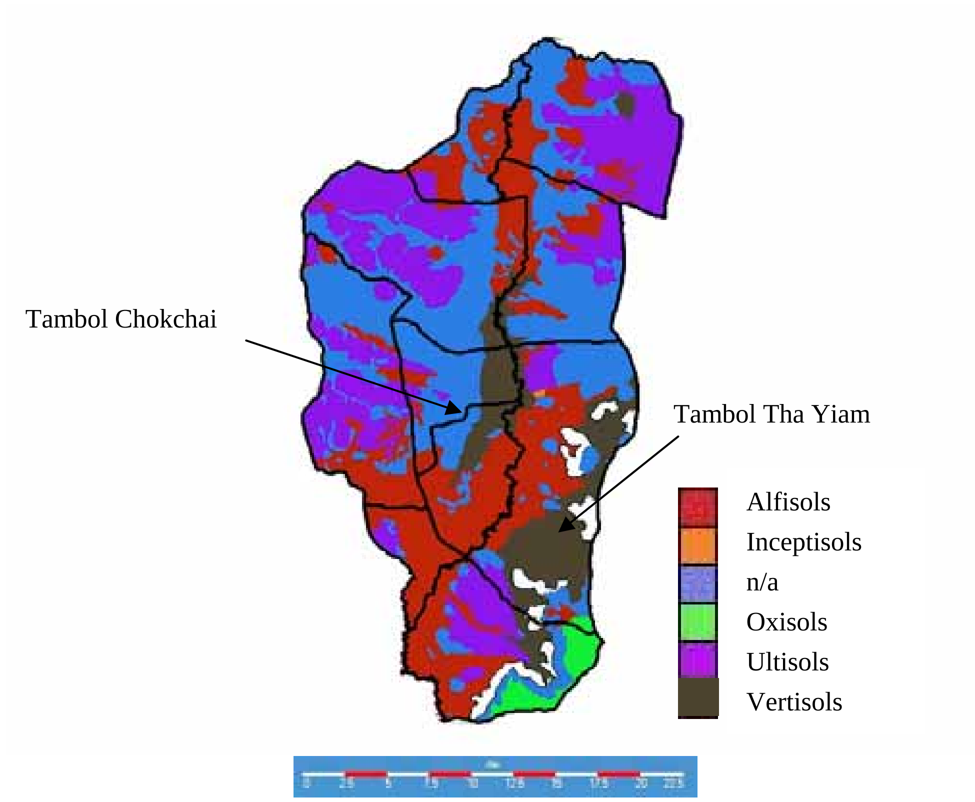

Figure A.4 Map of vertisol soils in Chokchai district showing the locations where soil samples were collected; Tambol Chokchai and Tambol Tha Yiam.

APPENDIX B

X-RAY DIFFRACTION SPACINGS OF PHYLLOSILICATES

Table B.1 Diagnostic X-ray diffraction maxima obtained from (001) planes of a few common phyllosilicates as related to sample treatment (Whittig and Allardice, 1986).

Diffraction Spacing (Å)	Mineral (or minerals) indicated
	Mg-saturated, air-dried
14.0-15.0	Smectite, vermiculite, chlorite
9.9-10.1	Mica (illite), hallosite
7.2-7.5	Metahallosite
7.15	Kaolinite, chlorite (2nd-order maximum)
	Mg-saturated, glycerol solvated
17.7-18.0	Smectite, vermiculite, chlorite
14.0-15.0	Vermiculite, chlorite
10.8	Hallosite
9.9-10.1	Mica (illite), hallosite
7.2-7.5	Metahallosite
7.15	Kaolinite, chlorite (2nd-order maximum)
	K-saturated, air-dried
14-15	Chlorite, vermiculite (with hydroxyl interlayer)
12.4-12.8	Smectite
9.9-10.1	Mica (illite), hallosite, vermiculite (contracted)
7.2-7.5	Metahallosite
7.1-7.3	Serpentine
7.15	Kaolinite, chlorite (2nd-order maximum)
	K-saturated, heated (550^{o}C)
14.0	Chlorite
9.9-10.1	Mica, vermiculite (contracted), smectite (contracted)
7.1-7.3	Serpentine
7.15	Chlorite (2nd-order maximum)

Table B.2 Diagnostic diffraction spacings of layer silicates and other common mineral present in the soil. The basal spacings of layer silicates are for Mg-saturated glycerol-solvated specimens. The most diagnostic peaks are indicated by bold face type (Jackson, 1965).

Mineral	**Diffraction spacing (Å)**
Kaolinite	7.15, 3.57, 2.38
Halloysite	10.7-10.0, 7.6*, 3.40
Antigorite and related serpentine minerals	7.3, 3.63, 2.41
Mica, Illite	10.1, 4.98, 3.32
Attapulgite	10.2-10.5, 4.49, 2.62
Vermiculite	14.4, 7.18, 4.79, 3.60
Chlorite	14.3, 7.18, 4.79, 3.59, 2.87, 2.39
Montmorillonite	17.7, 8.85, 5.90, 4.33, 3.54
Quartz	3.34, 4.26, 1.82
Dolomite	2.88, 2.19, 1.80
Calcite	3.04, 2.29, 2.10
Aragonite	3.40, 1.98, 3.27
Anatase	3.51, 1.89, 2.38
Rutile	3.26, 1.69, 2.49
Gypsum	7.56, 3.06, 4.27
Feldspars	3.18-3.24
Amphiboles	8.40-8.48
Gibbsite	4.85, 4.37, 2.39
Geothite	4.18, 2.45, 2.70
Hematile	2.69, 2.59, 1.69
Ilmenite	2.74, 1.72, 2.54

* Partially dehydrated Halloysite

Table B.3 Standard diffraction spacing of minerals common to soils or occasionally found in soils (Jackson, 1965).

d/n spacing, Å	Order	Mineral
32	1	Regular interstratification of chloride + montmorillonite
28	1	Regular interstratification of montmorillonite + mica or chlotide + vermiculite
24	1	Regular interstratification of vermiculite + mica
19.2-19.5		Random mixture of 10 + 17.7Å, etc.
17.7	1	Montmorillonite, glycerol solvated
17.2	1/1	Random 50:50 mixture of 10 + 17.7Å
17.0	1	Montmorillonite, ethylene glycol solvated
14.2	1	Chloride or vermiculite
13.3	1/1	Random 50:50 mixture of 10 + 14Å
11.0	1	Halloysite, glycerol solvated
10.2		Attapulgite
10.0	1	Illite, micas
9.5	1/2	Random 60:40 mixture of 10:17.7Å
9.2	1	Talc
9.2	1/2	Random 40:60 mixture of 10:17.7Å
9.1	1	Pyrophyllite
8.85	2	Montmorillonite
8.6	1/1	Random mixture of 7 + 10Å
8.40-8.48	1	Amphiboles
7.3	1	Antigorite, chrysotile

Table B.3 (Continued)

d/n spacing, Å	**Order**	**Mineral**
7.25-7.35	1	Partially dehydrated halloysite
7.2	1	Kaolinite, meta-halloysite
7.0-7.2	2	Chloride or vermiculite
6.3-6.45		Feldspars
6.23		Boehmite
5.0	2	Muscovite
4.7-4.9	3	Chlorite
4.83		Gibbsite
4.6-4.7		Talc
4.6	3	Vermiculite
4.57		Pyrophyllite
4.45-4.60	110	Montmorillonite, vermiculite, muscovite, Illite
4.45-4.46	110	Kaolinite
4.42	110	Meta-halloysite
4.34		Gibbsite
4.29		Gypsum
4.21		Quartz
4.15		Goethite
4.05		Cristobalite
3.66	3	Halloysite, glycerol solvated
3.59-3.64	2	Antigorite, chrysotile
3.57-3.58	2	Metahalloysite, kaolin
3.54	5	Montmorillonite, glycerol solvated
3.52-3.58	4	Chlorite
3.50-3.55	4	Vermiculite

Table B.3 (Continued)

d/n spacing, Å	Order	Mineral
3.47		Anatase
3.35		Quartz
3.33	3	Muscovite, illite
3.21-3.28		K-feldspars
3.12-3.25		Plagioclase, feldspars
3.1-3.25		Hornblende
3.15		Gypsum
3.03		Calcite
2.88		Dolomite
2.87		Gypsum
2.77-2.83		Apatite
2.73		Hornblende
2.69-2.73		Apatite
2.69		Hermatite
2.54		Ilmenite
2.53		Magnetite
2.52		Olivine
2.51		Hermatite
2.46		Olivine
2.43		Geothite
2.34		Boehmite
2.28		Calcite
2.19		Dolomite
1.92		Gypsum, calcite
1.88		Anatase

Table B.3 (Continued)

d/n spacing, Å	Order	Mineral
1.87		Calcite
1.85		Boehmite
1.81		Quartz
1.80		Dolomite
1.72		Ilmenite
1.69		Anatase
1.69		Hematite
1.61		Magnetite
1.53-1.55	060	Biotite, chloride (trioctahedral)
1.50	060	Muscovite (dioctahedral)
1.49	060	Kaolinite
1.48		Magnetite
1.44		Hornblende

APPENDIX C

XRD PATTERN OF Na-MONTMORILLONITE (SWy-2)

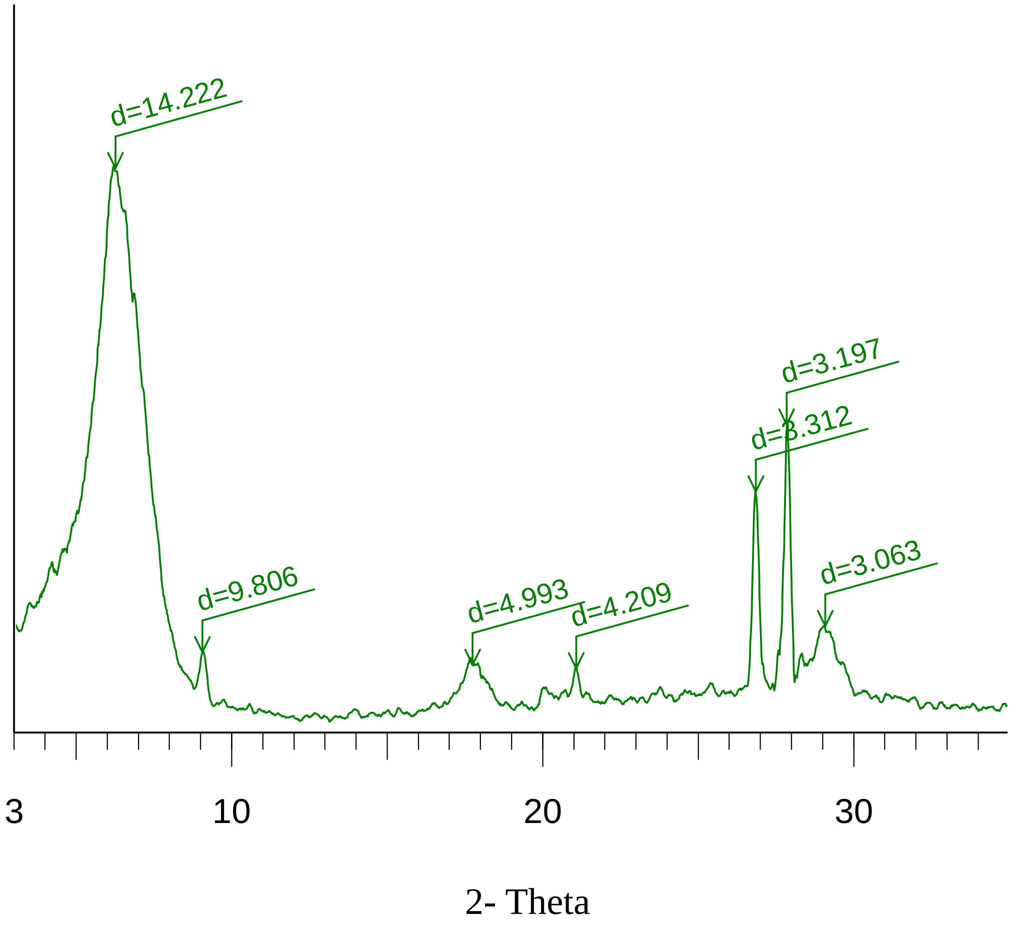

Figure C.1 XRD pattern of commercial montmorillonite (SWy-2) from the source Clays Repository, Crook county, Wyoming, USA .

APPENDIX D

THERMAL ANALYSIS OF THE SEPARATED FINE CLAY SAMPLES AND Na-MONTMORILLONITE (SWy-2)

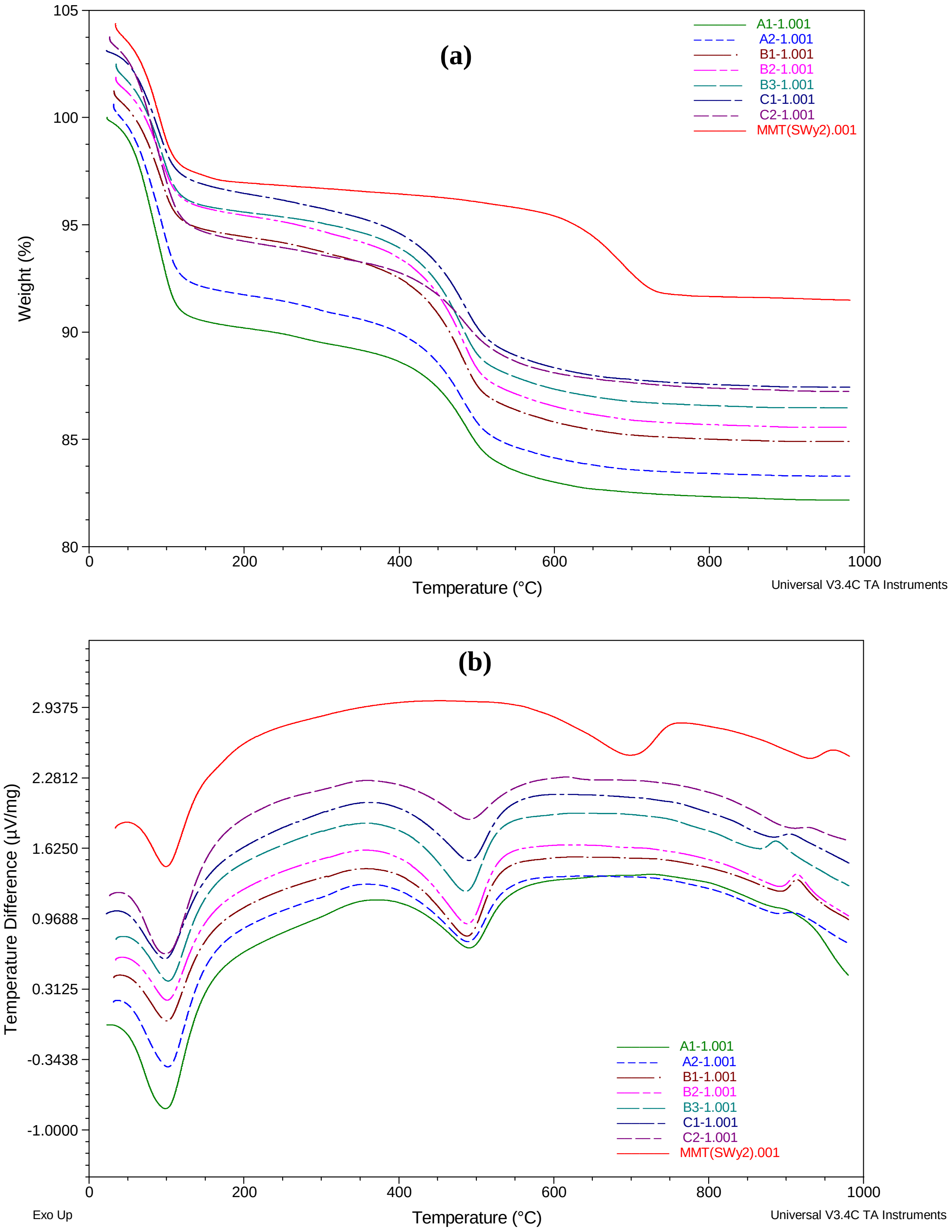

Figure D.1 Thermal analysis of the separated fine clay and commercial Na-montmorillonite (SWy-2); (a) TGA curves and (b) DTA curve.

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2. "Extraction and characterization of Montmorillonite in clay from Lopburi province, Thailand", (with Tritaporn Choosri), The 30th Congress on Science and Technology of Thailand, 19-21 October, 2004, Impact Exhibition and Convention Center, Muang Thong Thani, Faculty of Science, Srinakarinwirot University, Thailand.