Chapter 2
Experimental

2.1 Sampling of representative raw Lampang clay

The representative raw Lampang clay was obtained from the Thai-Kaolin Co.,LTD. Raw Lampang clay from Kao-Pangka, transported to the treatment plant, was sampled from many points in the storage silo. These samples were mixed together and this composite sample was deemed to represent raw Lampang clay.

2.2 Preparation of raw Lampang clay

Two tons of representatives raw Lampang clay was crushed and classified by grain size into 3 categories: clay with particles smaller than 63 microns, clay with particles smaller than 40 microns, and clay with all particles smaller than 10 microns. The two coursest samples were obtained by means of standard sieves; the finest sample by an air classifier. Four samples of Lampang clay are characterized. The symbol "U" means unfractioned Lampang clay, "C" means course sieved with all particles smaller than 63 microns, "M" means medium sieved with all particles smaller than 40 microns and "F" means the finest fraction with all particles smaller than 10 microns. Each of these fractions are characterized and compared with the unfractioned clay.

All samples are characterized in this study. After they are evaluated the most suitable sample is selected for further study and the best options for further refinement are identified.

2.3 Characterization and evaluation of the dry ceramic clay-mineral.

2.3.1 Particle size distribution

For a description of the standard technique for particle size distribution see "Whitewares"[5]. Here one can find the details. In brief, the distribution of course particles can be obtained with standard sieves, fine particles may require centrifugation or even optical methods. The cited reference describes these techniques in detail.

The present work was performed by using a Laser particle size analyzer, Sympatec HELOS H0392 by DIN-66141[6] "Darstellung von Korn-(Teilchen-) grossenverteilungen".

2.3.2 Chemical analysis

For a description of the standard techniques for chemical composition see "Whitewares"[5]. In brief, the chemical analysis of a clay or other ceramic material is usually expressed in terms of percentage composition of constituent oxides. This type of chemical analysis was originally obtained by "wet" methods, but now X-ray fluorescence (XRF) technique is both fast and accurate and was used here. Chemical analysis by means of atomic absorption spectroscopy (AAS) is also a good method for chemical analysis of mineral sample.

The present work was performed by using a Atomic absorption spectroscopy, Shimadzu, AA-640-13 and Spectrometer, Lambda 19.

2.3.3 Mineralogical composition

For a description of the standard technique for mineral composition see "Whitewares"[5]. In brief, mineral composition of a ceramic material is carried out using X-ray diffraction (XRD). Approximate amounts of these minerals also may be obtained with XRD. Quantitative estimation is limited in accuracy.

The present work semi-quantitative mineralogical phase analysis was performed by means of X-ray diffractometer, Phillips, PW 3710.

2.3.4 Thermal analysis

Thermal investigations can give information about the type of mineral present in the sample under investigation. Two types of thermal analysis are of interest to the ceramist, differential thermal analysis (DTA), and thermogravimetric analysis (TGA).

2.3.4.1 Differential thermal analysis (DTA)

For a description of the standard technique for DTA see "Whitewares"[5]. In brief, temperature changes are continuously monitored in a sample while its temperature is raised at a controlled rate. If the sample undergoes a reaction involving absorption of heat, its temperature will be less than that of a blank and this is revealed by an endothermic trough in the curve which results when thermocouple voltage (caused by temperature differences) is

plotted against time. If the reaction involves evolution of heat, the sample will be at a higher temperature than the blank, and an exothermic peak is seen.

The present work was performed by using a Differential thermal analyzer, Shimadzu, DTA-50 by DIN-51007[7]: "Differenzthermoanalyse".

2.3.4.2 Thermogravimetric analysis (TGA)

For a description of the Thermogravimetric analysis (TGA) see "Whitewares"[5]. In brief, this test involves the measurement of weight changes in a sample while it is being continuous heated. Changes in sample materials are recognized by the amount of weight lost and the temperature at which this loss occurs.

The present work was performed by using a Differential thermal analyzer, Shimadzu, DTA-50 by DIN-51006[8]: "Thermische Analyse".

2.3.5 Cation exchange capacity

For a description of the standard technique for cation exchange capacity measurement see "Whitewares"[5] for details. In brief, Cation Exchange Capacity was obtained using the ammonium acetate method, more details can be found in TGL-24747[9]: "Bestimmung der Kationenaustauchkapazitat nach der Ammoniumacetatmmethode", and DIN-51722[10]: "Bestimmung des Stickstoffgehaltes".

The chemicals used in this work are as follows :

- CH_3COO solution, 1 N, pH=7
- KOH solution, 30% (386.4 g KOH / 1,000 ml H_2O), Fluka Chemie AG, Lab grade
- NaOH solution, 0.1 N
- Methylred, 0.2% conc., pH 4.4-6.2 (0.178 g Methylred / 100 ml 60% Alcohol), Fluka Chemie AG, Lab grade
- Concentrated HCl
- Triethylamin hydrochloride
- Hydroxylamin hydrochloride
- NaOH solution, 20% (243.8 g NaOH / 1,000 ml H_2O), Fluka Chemie AG, Lab grade

- Ammonium solution, pH=10 (54 g NH_4Cl + 352 ml NH_4OH (conc.) · H_2O → 1 l.), Fluka Chemie AG, Lab grade
- Fluorexon
- Thymolphtalexon
- Catalyst mixture : 842 mg K_2SO_4 + 26 mg Selen powder + 132 mg $HgSO_4$, Fluka Chemie AG, Lab grade

2.3.6 Surface area

For a description of the standard techniques for determination of surface area see "Whitewares"[5]. In brief, surface area can be obtained by either of two methods – permeability to a standard a fluid or adsorption of a gas (or solution) on to the surface of the powdered material. Also, it is possible to obtain approximations of surface area by strip integration of a particle size distribution curve. Conversely, it is possible to calculate an approximate average particle size from surface area data. The cited reference describes these techniques in detail. The present work used specific surface area measured with a BET theory and measured by Area Meter II in accordance with DIN-66132[11]: "Bestimmung der spezifischen Oberflache von Feststoffen durch Stikstoffadsorption" and DIN66133[12]: "Bestimmung der Porenvolumenvertailung und der spezifischen Oberflache von Feststoffen durch Quecksilberintrysion"

2.3.7 Rheology of the clay slip

For a description of the standard technique for measuring rheological behaviour of clay and clay slips see "Whitewares"[5] for details. In brief, rheological behaviour can be obtained as viscosity, fluidity, thixotropy, deflocculant demand and casting control. The cited reference describes appropriate techniques in details.

The present work obtains rheological information as viscosity and shear stress curves after optimal deflocculating with Na_2CO_3. Shear rate and the corresponding changes in other properties was obtained with a Rotation-Viscometer, VT-550 in accordance with DIN-53019 : "Messung von Viskositaten und Fliesskurven mit Rotations viskosimetern mit Standardgeometrie"[13] and DIN-52312[14]: "Messung der Viskositat". The deflocculant demand study was in accordance with TGL-14932[15]: "Bestimmung des optimalen Elektrolytgehaltes

und der Thixotropiezahl". The present work was use as the deflocculant, Na_2CO_3 from Fluka Chemie AG, Lab grade.

2.3.8 Property of the moist clay

2.3.8.1 Plasticity

For a description of the standard techniques for plasticity see "Whitewares"[5] for details. In brief, the plasticity can be obtained with the "Pfefferkorn Test". The cited reference describes this technique in detail. The present work measured Plasticity behavior as flow stress and maximum deformation which depends on the moisture content.

The present work was performed by using the TIRA tester, series 2420 with "Beitrag zur rheologischen Charakterisierung bildsammer keramischer Massen"[16], Keram. Ztscher. 36 (1984) 10, s. 524-528[17] and TGL-18887[18]: "Bestimmung des Deformationsverhaltnisses zur Beurteilung der Verabeitungsfeuchte". See also Berichte de DKG: "Messung der Plastizitat"[19].

2.3.8.2 Shrinkage

For a description of the standard techniques for shrinkage see "Whitewares"[5] for details. In brief, shrinkage can be obtained as wet-to-dry shrinkage, dry-to-fired shrinkage and wet-to fired shrinkage. The cited reference describes appropriate techniques in detail.

The present work was performed by using DIN-51045 part-1[20], DIN-51066[21] for wet-to-dry shrinkage. Wet-to-fired shrinkage was measured in accordance with DIN-51066 part-2[22] and DIN-51045 part-2[23].

2.3.8.3 Modulus of rupture as a measure of strength

For a description of the standard technique for strength measurement see "Whitewares"[5]. Here one can find the details. Briefly, strength can be obtained as compressive strength or bending strength. The cited reference describes these techniques.

The present work measured dry strength and fired strength as defined by three point bending strength was measured by TIRA tester 2420 according to DIN-51030[24]: Bestimmung der Trockenbiegefestigkeit, for dry strength and fired bending strength in accordance with DIN EN 100[25] and DIN-52292[26]: Bestimmung der Biegefestigkeit.

2.3.9 Properties of the fired clay

For a description of the standard technique for fired behaviors and properties of porcelain pottery see "Whitewares"[5]. Here one can find the details. In brief, the fired behavior and properties can be obtained as shrinkage, strength, density, porosity, water absorption, and whiteness. The cited reference describes these techniques in details.

The present work reports on various firing temperature in a heated SiC electric kiln, with a heating rate 5 K/min and 30 min soaking time at the final temperature. Shrinkage study followed "Total shrinkage" in accordance with DIN-51066[21] and DIN-51045 part-2[23]. Strength study followed "Bending strength" in accordance with DIN EN 100[25] and DIN-52292[26] with TIRA tester 2420. Density was measured in accordance with DIN ISO 5018[27], "Bestimmung der Dichte" and DIN-51065[28], "Bestimmung der Rohdichte" by Autoscan-33 Porotimeter, series AccuPyc-1330 V2.01. Porosity is studied by water adsorption and open porosity is studied in accordance with DIN-51056[29], "Bestimmung der Wasseraufnahme und der offenen Porositat". Whiteness is reported in the comparison to a $BaSO_4$ plate with a 464 nm. Filter. Pressed test-pieces (15 mm^2 area) are made in an electric kiln with different final temperatures and in a tunnel kiln at a porcelain factory at 1385^{0}C. Measurements were made with a Lambda 19 Spectrophotometer.

2.4 Methods to refine the raw material.[30-56]

In general, there are by 2 ways to refine clay, physical refinement and chemical refinement.

For a description of physical refinement see "Wet Preparation of Kaolin (China Clay)"[30-53]. In brief, the physical refinement can be done by selection according to particle size and by magnetic separation. The cited reference describes these techniques in detail. The present work used wet standard sieves and a Turbo classifier, series TC-15M for size classification, a magnetic separator with 5 Tesla power at AKW (Amberger Kaolinwerk - Eduard Kick GmbH & Co. KG) was used for magnetic separation.

For a description of chemical refinement see "Tonminerale und Tone"[54], "Clays and Ceramic Raw Materials : Methods used for the identification and characterization of clays"[55], the dithionite method for the removal of oxides of iron, "Empfindliche und schnelle Methode zur Bestimmung von Fe (II) und Gesamteisen in Natron- Kalk- Silikat- Glasern"[56]. The cited

reference describes these techniques in details. The present work used the dithionite method to remove the iron oxide from the surface of clay particles.

2.5 Uses of Lampang clay

2.5.1 Application for porcelain pottery production.[57-70]

The selected sample is evaluated for the possibility of using it to make porcelain pottery. For a description of the "Porcelain-Raw Materials, Processing, Phase Evolution, and Mechanical Behavior" see William M.Carty and Udayan Senapati, *J.Am.Ceram. Soc.*, **81** [1] 3-20 (1998)[57]. In brief, porcelain pottery is composed primarily of clay, feldspar, and quartz. Porcelains are fired to high temperature to form mixtures of glass and crystalline phases. The cited reference describes the raw materials and processing for making porcelain pottery. The usual problem is iron content in the clay which results in an off white color after firing. The present work used Lampang clay and Lampang stone as the main components for the porcelain body. The green porcelain ware was fired in an electric laboratory kiln under an ordinary oxidation atmosphere and in a gas industrial kiln under reduction conditions. After firing, the samples were evaluated.

2.5.2 Application of the remaining part of Lampang clay for production of floor tile is explored.[71]

The part of Lampang clay that can not be use to make porcelain is studied for suitability for use in making floor tile. For a description of "Wall and Floor tile" see M.Drews, Ceramic Monographs – Handbook of Ceramics, 1983[71]. In brief, floor tile consist of clay, feldspar, and quartz. Floor tile is fired to form a mixture of glass and quartz phases. The cited reference describes the raw materials and processing for floor tile. The present work used the fraction left after making porcelain from Lampang clay. Lampang clay and Lampang stone together with secondary clay such as Mae-tan clay were mixed and used to produce floor tile body. The material was fired in an electric laboratory kiln under oxidation atmosphere not higher than 1250^{0}C.