

CHAPTER 3

MATERIALS AND METHODS

3.1 Locations and depths of testing samples.

In this study, 48 soil samples were selected from three locations from the north, where the samples were taken from Pakget, Lad Prout, and Bang Sue. Three locations from the east, samples were taken from Asoke-Din Daeng Road, Lumpini Park and Tha Rue. Two locations from the west, from Bang Kun Prom and Klong Sarn and two locations from the south of Bangkok from Bangna and Phrapradaeng. The samples were mostly collected at the elev. -1.50 to -17.00 m. Details of sampling locations and depth are plotted on the map shown in Figure 2 and Table 1 respectively.

3.2 Particle size distribution

3.2.1 Testing procedure.

(a) An appropriate amount of soil (about 50-100 gm.) was taken from the soil sample: and put into a beaker. Distilled water was added and stirred until the soil became slurry, more distilled water would be added if necessary. The slurry was poured in sieve No.200, distilled water was again added on the sieve No.200 which containing the slurry, in order to ensure that sand in the slurry was absolutely separated. Then, the residue on the sieve No.200, which was considered to be sand, was weighed to determine the sand content.

(b) Pipette method was then used to determine clay and silt fraction. The passed slurry from sieve No.200 was oven dried. Then 10 gm, taken from the oven dried soil, was ground and put into a beaker. Added 20 cc. dispersing agent (Sodium Metaphosphate or Calgon) into the soil in the beaker stirred.

T A B L E I

Location, Depth and Laboratory Code of Testing Samples

No.	Depth	Location	Lab Code
1.	1.40-1.50	Lumpini Park	L1
2.	3.50-3.60	"	L2
3.	4.10-4.20	"	L3
4.	4.80-4.90	"	L4
5.	5.80-5.90	"	L5
6.	9.00-9.60	Asoke-Dindaeng Road	AS1
7.	12.00-12.60	"	AS2
8.	13.50-14.10	"	AS3
9.	1.50-2.10	Lad Prout	LP1
10.	3.00-3.60	"	LP2
11.	4.50-5.10	"	LP3
12.	6.00-6.60	"	LP4
13.	7.50-8.10	"	LP5
14.	9.00-9.60	"	LP6
15.	10.50-11.10	"	LP7
16.	12.00-12.60	"	LP8

Table I (Cont.)

No.	Depth	Location	Lab Code
17.	3.00-3.50	Tha Rue	TH1
18.	4.50-5.00	"	TH2
19.	1.50-2.10	Bang Sue	BS1
20.	4.50-5.10	"	BS2
21.	9.00-9.60	"	BS3
22.	10.50-11.10	"	BS4
23.	13.50-14.10	"	BS5
24.	1.50-2.10	Thai Sugar (Phrapradaeng)	TS1
25.	3.00-3.60	"	TS2
26.	6.00-6.60	"	TS3
27.	9.00-9.60	"	TS4
28.	13.50-14.10	"	TS5
29.	15.00-15.60	"	TS6
30.	4.50-5.25	Siam Cement (Pakget)	S 1
31.	6.00-6.75	"	S 2
32.	7.00-7.75	"	S 3

Table I (Cont.)

No.	Depth	Location	Lab Code
33.	2.00-2.75	Siam Cement (Pakget)	S 4
34.	3.00-3.50	Bank of Thailand(Bang Kumpunn)	B 1
35.	8.00-8.50	"	B 2
36.	10.50-11.00	"	B 3
37.	1.50-2.10	Bangna (Bangna Trad K.M.4)	BA1
38.	4.50-5.10	"	BA2
39.	6.00-6.50	"	BA3
40.	9.00-9.50	"	BA4
41.	13.50-14.00	"	BA5
42.	16.50-17.00	"	BA6
43.	1.50-2.10	Klong Sran (Nishimatsu Station)	NI1
44.	4.50-5.10	"	NI2
45.	6.00-6.60	"	NI3
46.	7.50-8.10	"	NI4
47.	9.00-9.60	"	NI5
48.	12.00-12.60	"	NI6

All the solution from the previous step was transferred into a graduate. Distilled water was added to 1,000 ml. volume. Recorded room-temperature, stirred the solution, initial time was immediately recorded after stirring. From Stoke's Law, time required by the solution to obtain 5 cm. sediment of silt fraction is calculated. After 5 cm. sediment of silt fraction was reached, extract 20 cc. of the solution above the 5 cm. sediment by a pipette. The 20 cc. solution was then oven dried to determine weights of clay and calgon. Weight of clay could be determined when the calgon weight was known.

3.3 Clay mineral identification

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3.3.1 Principle of X-ray diffraction.

Since the clay fraction (particle size less than 2μ) is normally composed of a mixture of secondary minerals with some primary minerals. The X-ray diffraction technique was used to identify the mineralogical composition of the clay samples because this method is very useful for studying the mixed crystalline portion of clay. X-ray diffraction method is used to observe spacing and intensity.

The principles of X-ray diffraction, as applied to clay, is when X-ray beam strikes a crystal. The rays penetrate and some scattered from many successive planes within crystal. Because each crystal contains planes of atoms which are separated by a constant distance which is called interplanar spacing. From Bragg's Law the interplanar spacing can be determined as follows.

$n\lambda$	=	$2d \sin \theta$
Where λ	=	X-ray wave length (for Cobalt = 1.78890°A)
θ	=	Angle between the X-ray beam and atomic planes
d	=	The distance between successive identical planes of atoms in the crystal
n	=	Order of reflection (1, 2, 3----etc)

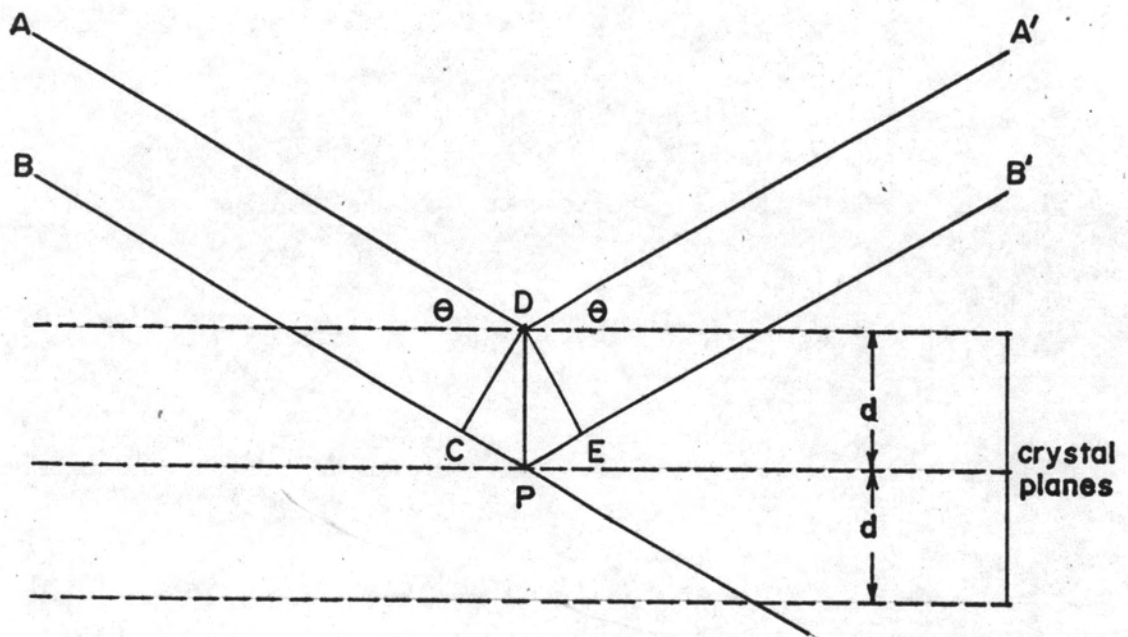
3.3.2 Preparation of samples

The clay fraction ($< 2\mu$) was separated from silt by repeated sedimentation and siphon at the appropriated time. The clay suspension was then flocculated with MgCl_2 . A portion of clay was treated according to the method of Jackson (1956) to remove exchangeable cations. It was then divided into two parts for K and Mg saturation and their films were prepared by drying a suspension of the clay on a glass microscope slide.

3.3.2.1 Procedure for separation of particle size fractions.

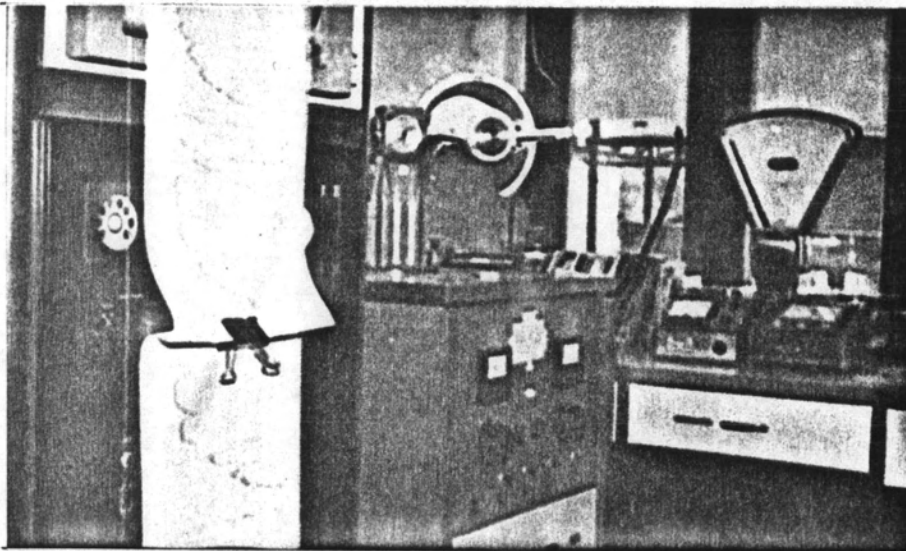
(1) Placed 10 gm. of soil in a 100 ml. graduate add 30 ml. distilled water, and added 15 ml. of 5% NaPO_3 (Sodium metaphosphate or calgon). Then stirred by glass rod until the solution was well mixed and let it stand overnight.

(2) The suspension from the previous step was stirred in an electric mixer about 3 minutes.

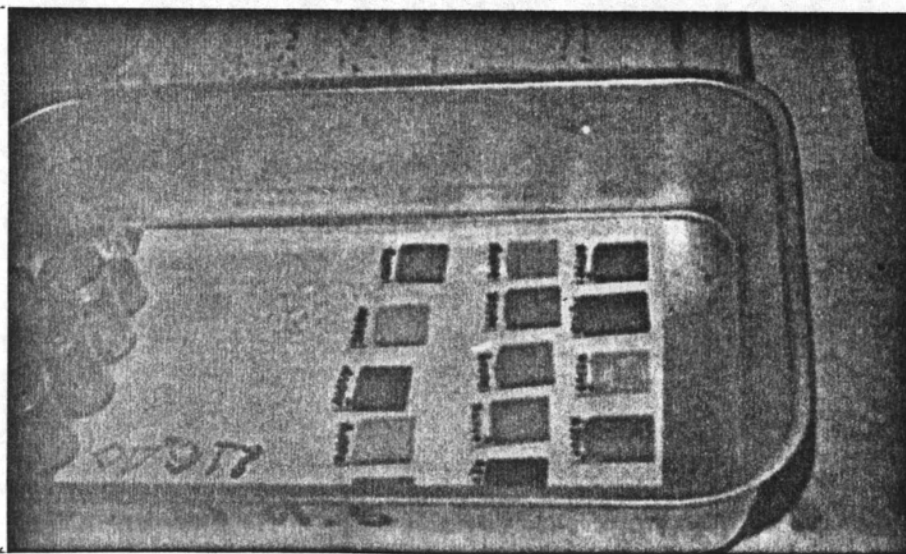


Diffraction from crystal planes according to Bragg's law, $n\lambda = 2d \sin \theta$

FIG 3.



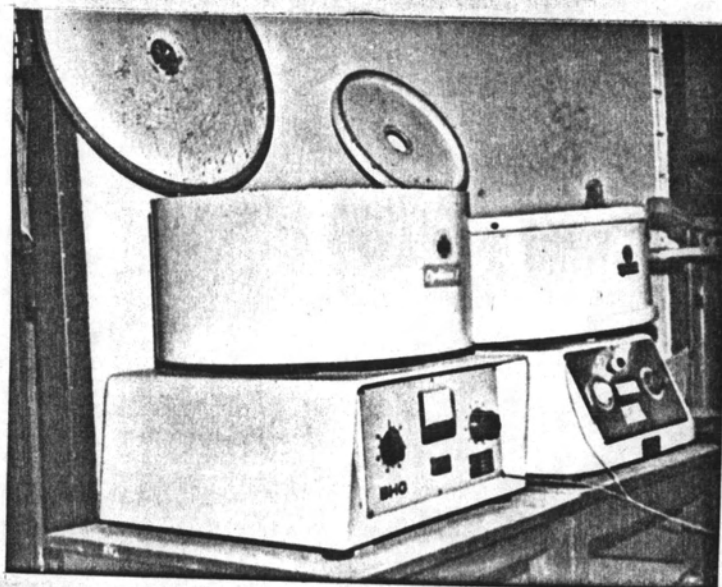
X-Ray Diffractometry Philips Type PR 2262A/00
Fe-Filtered; CoK-Radiation Operating Rate 20 KV, 10 mA



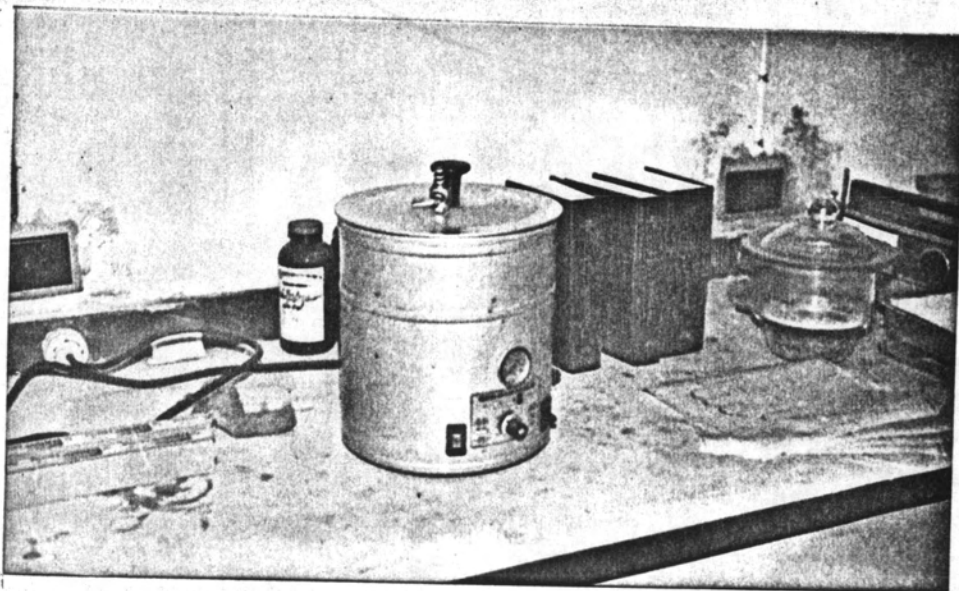
Glass Plate

FIG 4.

FIG 5.



Centifuge Apparatus
Optima I Type BHG 702



Vacuum Desiccator
Ser No. 11-W-2

(3) While the soil and water were being mixed, filled a 1,000 ml. cylinder with distilled water and added enough distilled water to bring the level to 1,000 ml. Calculated the sedimentation time of 2 micron diameter by Stokes' Law. Separated clay fractions from the sand and silt fraction by Suphon.

3.3.2.2 The procedures for magnesium and potassium saturated clay samples for X-ray diffraction are given as the following steps.

- (1) For clay fractions flocculate by adding 5-6 drops of 1 : 1 acetic acid.
- (2) Added 1 ml. of 1N $MgCl_2$ to bring the sample to be Mg-saturated. Added 1 ml. of 1N KCl to bring the sample to be K-saturated. The suspension was thoroughly mixed and centrifuged.
- (3) The solution from the centrifuge was disregarded. Add small volume (10 ml.) of distilled water to the centrifuge.
- (4) To remove chloride by washing with absolute alcohol 95% (ethanol). To ensure the chloride was completely removed check by adding few drops of silver nitrate ($AgNO_3$).
- (5) For silt fractions was washed with distilled water and then was washed with absolute alcohol 95% (ethanol).
- (6) Glass - plate method for oriented aggregated. Add sufficient water to the sample to make a suspension of approximately 2 ml. volume. Thoroughly mixed the suspension to ensure complete dispersion. Extracted the suspension with a pipette, and carefully transfer it to

a glass microscope slide and resting on a level surface. Let the suspension dry completely on the slide before the sample was analysed.

- (7) A glass microscope slide of magnesium saturated clay was added with a drop of ethylen glycol to make a glass slide of magnesium saturated with ethylen glycol.
- (8) A glass microscope slide of potassium saturated is heated to 550°C for 2 hours.

3.3.3 Data interpretation technique.

The criteria for differentiation of silicate layers is to identity by the diagnostic diffraction maxima, of the X-ray patterns obtaining from the specially treated soil samples. The diffraction maxima obtained, represents the angle between the X-ray beam and atomic planes (designated by Θ). By Bragg's Law, the angle Θ can be converted to interplannar spacing (d). Conversion table of angle Θ to d spacing is given in Appendix C (for cobalt radiation).

Once the d - spacing is determined, identification of minerals in the soil samples can be obtained by 2 methods. First method is to compare the diffraction maxima of the soil samples with the standard maxima obtained from of the known minerals. Second method is to compare the d spacings with those spacings in Tables 2, 3 which were prepared by Warshaw and Roy in 1961.

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TABLE 2

X-Ray diffraction spacing obtained from (001). Planes of layer silicate species as related to sample treatment.

Diffraction spacing. (A)	Mineral (or minerals) indicated
14 - 15	Mg. -saturated, air - dried
	Montmorillonite, Vermiculite, Chlorite
9.9 - 10.1	Mica (illite) halloysite
7.2 - 7.5	Metahalloysite
7.15	Kaolinite, Chlorite (2 nd order max.)
17.7 - 18.0	Mg. -saturated, (Ethylen Glycol)
	Montmorillonite
14 - 15	Vermiculite, Chlorite
10.8	Halloysite
9.9 - 10.1	Mica (illite)
7.2 - 7.5	Metahalloysite
7.15	Kaolinite, Chlorite (2 nd order max.)
14 - 15	K - saturated, air - dried
	Chlorite, Vermiculite (with inter layer aluminum)
12.4- 12.8	Montmorillonite
9.9 - 10.1	Mica (Illite), Halloysite, Vermiculite (contracted)
7.2 - 7.5	Metahalloysite
7.15	Kaolinite, Chlorite (2 nd order max.)
14	K - saturated, heated (500°C)
	Chlorite
9.9 - 10.1	Mica Vermiculite (contracted) montmorillonite (contract)
7.15	Chlorite (2 nd order max.)

TABLE 3

Diagnostic diffraction spacings of layer silicates and other common minerals 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.

Mineral	Diffraction Spacing (A)
<u>Kaolinite</u>	<u>7.15, 3.57, 2.38</u>
<u>Halloysite</u>	<u>10.7-10.0, 7.6, 3.40</u>
<u>Antigorite and related serpentine minerals</u>	<u>7.3, 3.63, 2.42</u>
<u>Mica, Illite</u>	<u>10.1, 4.98, 3.32</u>
<u>Attapulgit</u>	<u>10.2-10.5, 4.49, 2.62</u>
<u>Vermiculite</u>	<u>14.4, 7.18, 4.79, 3.60</u>
<u>Chlorite</u>	<u>14.3, 7.18, 4.79, 3.59, 2.87, 2.39</u>
<u>Montmorillonite</u>	<u>17.7, 8.85, 5.90, 4.33, 3.54</u>
<u>Quartz</u>	<u>3.34, 4.26, 1.82</u>
<u>Dolomite</u>	<u>2.88, 2.19, 1.80</u>
<u>Calcite</u>	<u>3.04, 2.29, 2.10</u>
<u>Aragonite</u>	<u>3.40, 1.98, 3.27</u>
<u>Anatase</u>	<u>3.51, 1.89, 2.38</u>
<u>Rutile</u>	<u>3.26, 1.69, 2.49</u>
<u>Gypsum</u>	<u>7.56, 3.06, 4.27</u>
<u>Feldspars</u>	<u>3.18-3.24</u>
<u>Amphiboles</u>	<u>8.40-8.48</u>
<u>Gibbsite</u>	<u>4.85, 4.37, 2.39</u>
<u>Goethite</u>	<u>4.18, 2.45, 2.70</u>
<u>Hematite</u>	<u>2.69, 2.59, 1.69</u>
<u>Ilmenite</u>	<u>2.74, 1.72, 2.54</u>

Table 3 from "Soil Clay Mineralogy by G.I. Rich, G.W.Kunze,
p.p 254

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Most minerals commonly found in the clay fraction are characterized by the basal spacing as following:

Kaolinite Basal spacing $7.15-7.20^{\circ}\text{A}$ which also corresponds to the second order reflection of chlorite. On heating at about $500-550^{\circ}\text{C}$ the crystallinity of kaolinite is destroyed.

Halloysite Basal spacing of 7.6°A and $10.0-10.7^{\circ}\text{A}$ corresponds to metahalloysite and hydrated halloysite respectively. Brindloy (1955) reported that on heating to 400°C the spacing decreased to 7.2°A .

Montmorillonite, Vermiculite, Chlorite Basal spacing of approximately 14°A are obtained from these minerals when saturated with Mg. K-saturated, the spacing of montmorillonite slightly decreases from 14°A to 12.5°A founded by Walker (1949). Montmorillonite is simply identified by treating in the Mg-saturated condition with glycerol, resulting in a shift of the first order basal spacing to $17.7-18.0^{\circ}\text{A}$. Persistence of a 14°A line after treatment indicates vermiculite chlorite or both. Heating of a K-saturated sample at 500°C for a number of hours causes the spacing of montmorillonites and vermiculite to shift to $9-10^{\circ}\text{A}$. Persistence of a 14°A line after this treatment therefore strongly indicates chlorite.

Illite gives a spacing of 10°A which is not affected by heating treatment or ethylen glycerol.

Quartz and feldspars are primary minerals which are frequently present in clay size fraction. Quartz is characterized by strong reflection at 3.34 and 4.26°A whereas feldspars give a reflection line between $3.18-3.24^{\circ}\text{A}$.

From four patterns of the X-ray diffractograms of Mg-saturated, Mg-saturated with ethylene glycol, K-saturated and K-saturated with heat. Peaks in each pattern are representing their angles of reflection which will lead to each particular d-spacing by Bragg's Law. From the d-spacings obtained from the four patterns, the clay mineral can be identified by comparison with the Table 2, 3.

Example interpretation. For Mg-saturated pattern shows the peak approximately 14°A . Mineral can be either montmorillonite, vermiculite or chlorite. In pattern of Mg-saturated with ethylene glycol if the peak show about $17.7-18.0^{\circ}\text{A}$ the mineral is montmorillonite. Up to this state, we can identify montmorillonite from vermiculite and chlorite.

In order to identify vermiculite and chlorite, the patterns, obtained from the K-saturated soil samples, heated at 500°C , whose peaks show at the sample angle of diffraction (14°A). Then the mineral, presents is chlorite. But if the peak shifts from 14°A to $9.9-10.1^{\circ}\text{A}$; the mineral, presents, is vermiculite, illite or hallosite will show the peak range approximately $9.9-10.1^{\circ}\text{A}$ in Mg-saturated pattern. To separate illite from hallosite by notifying the peak in Mg-saturated with ethylene glycol if the peak changes to 10.8°A the mineral present is hallosite.

If the peak shows at $7.2-7.5^{\circ}\text{A}$ in Mg-saturated pattern the mineral present is metahallosite.

Peak shows approximately 7.15°A in Mg-saturated the peak can identify kaolinite or chlorite (2^{nd} order).

By notifying the peak in K-saturated and heating if the peak disappeared the minerals present is kaolinite. If the minerals present in chlorite (2nd order) the peak will stand in the same position. In the case the peak shows between 7-10^oA, it is a interstratification of layer clay minerals between 7^oA and 10^oA group.

Sometimes the peak shows between 10-14^oA it is a interstratification of layer clay minerals between 10^oA and 14^oA group.

Quantitative interpretation of diffraction pattern. The intensities of the maxima diffraction curves are related to the number of diffraction planes in a sample. From this relation causes a basis of semi quantitative estimation of clay minerals. The areas under the peaks in X-ray pattern with respect to the basal line are used the calculated the quantitative.

Supposed there are three peaks, sum of areas are called to 100 percent. Each area of the peak is compared with the total area. The quantitative interpretation of the X-ray diffraction pattern is only semi quantitative. Because there are many factors control the intensities of the pattern. The controlled fractors are particle sizes, crystal perfection, crystal orientation presence of amorphous substance and other fractors.

3.4 Determination of cation exchange capacity

Clay minerals have the property of adsorption of anions and cations. These ions remain in exchange state. The exchangeable ions are held around the outside of silica-alumina clay minerals structural units. Generally the exchange reaction does not effect the structure of silica-alumina units.

The exchange electrical charge may arise from any one or a combination of the five following factors:

1. Isomorphous substitution.
2. Surface disassociation of hydroxyl ions.
3. Absence of cation in the crystal lattice.
4. Absorption of anions.
5. Presence of organic matter.

Of these five possible causes the first isomorphous substitution is the most important.

The range of cation exchange capacity of the clay minerals after (Grim 1953) is given in the table following:

CATION - EXCHANGE CAPACITY OF CLAY MINERALS

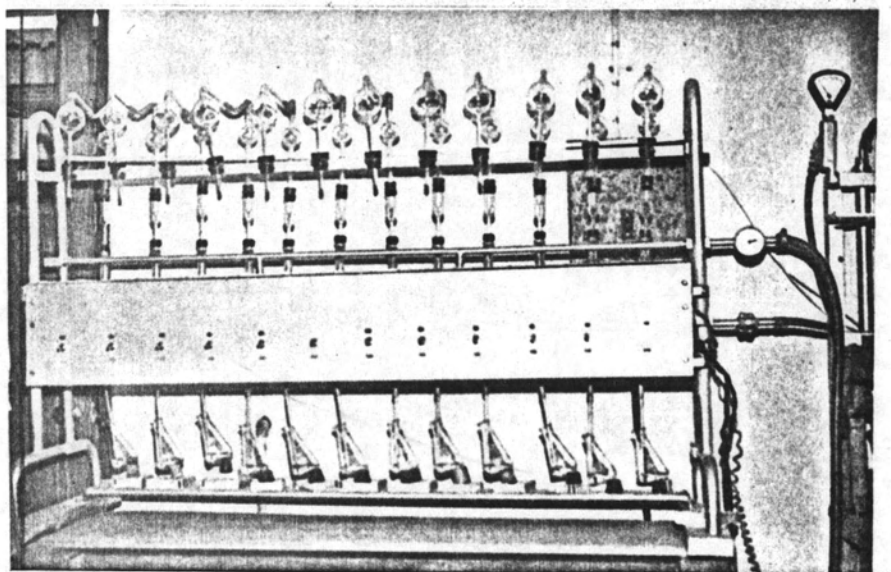
(in milliequivalent per 100 Grams)

Kaolinite	3 - 15
Halloysite 2H ₂ O	5 - 10
Halloysite 4H ₂ O	10 - 40
Montmorillonite	80 - 150
Illite	10 - 40
Vermiculite	100 - 150
Chlorite	10 - 40
Sepiolite-attapulgitite	20 - 30

(meq. = milliequivalents = 10^{-3} equivalent. An equivalent is the number of electronic charges in one mole of solution and equal 6×10^{23} Avogadro's number. An exchange capacity of 1 meq. per 100 gm. means that each 100 gm. of soil solids can exchange $1 \times 10^{-3} \times 6 \times 10^{23} = 6 \times 10^{20}$ electronic charges).

3.4.1 Determination method. The cation exchange capacity determination involves measuring the total quantity charge per unit weight of the material. There are many methods to determine the cation exchange capacity. These methods generally base on saturating the exchange complex with a given cation and then determining the total of the adsorbed cations. Three reagents commonly use for this purpose, are neutral (pH 7.0) of 1N ammonium acetate; alkaline (pH 8.2), 1N sodium acetate; and alkaline (pH 8.2), 0.5 barium chloride plus 0.2N trithanolamine solution. The first two methods can be used on both calcareous and noncalcareous soil. The third is used on acid soil where it is desired to determine both exchange capacity and amounts of exchangeable hydrogen. For this experiment, the author worked on the method of displacement and distillation for absorbed ammonium.

FIG 6.



Distillation Apparatus

3.4.1.1 The procedure for cation exchange capacity by the method of displacement and distillation for absorbed ammonium.

(1) Obtain soil samples containing all particles smaller than 2 mm. by sieving.

(2) Air dried 5 gm. of soil sample, smaller than 2 mm. Put into 500 ml. flask and added 50 ml. neutral, 1N NH_4OAc (pH7). Shaking the flask and let it stand overnight.

(3) The solution was filtered by Pyrex Buchner funnel with the aid of light suction. During this step one must be aware not to let the soil on the filter-paper become dry and crack. The soil was leached by neutral NH_4OAc about three times until no calcium was present in the effluent solution. (For the calcium test, a few drops of 1N NH_4Cl 10% ammonium oxalate, and diluted NH_4OH to 10 ml. of the leachate in a test tube and heat the solution to near the boiling point the presence of calcium is indicated by white precipitate or turbidity).

(4) Leach the soil four times with 1N NH_4Cl

(5) Leach the soil one time with 0.25N NH_4Cl .

(6) Leach the soil 5 times with 95% ethyl alcohol.

(7) Transferred the leachate to a new Pyrex Buchner funnel.

(8) Leach the ammonium saturated soil with 10% acidified NaCl until obtaining the volume of 300 ml.

(9) Transferred the solution to a 800 ml. Kjeldahl flask, add 25 ml. of 1N NaOH and distilled. Vapour from the solution was passed through a flask containing 0.1N HCl 25 ml., then added 10 drops of bromocresol green methyl red mixed indicator into the new flask. Titrated the residual chloric acid with 0.1 NaOH. The colour change from bluish green through bluish purple to pink at the end point run the blanks on the reagents. Corrected the titration

figure for the blanks and calculate the milliequivalents of ammonium in 100 gm. of soil by the formula.

$$\text{meq. exchange capacity per 100 gm.} = \frac{\text{ml. versene} \times N \times 100}{\text{sample weight in gm.}}$$

where ml. versene = (Blank - Titration) in ml.
 N = Standard Normal of NaOH
 = 0.10083N

3.5 Chemical Analysis of Bangkok clay

3.5.1 Determination Method

It is generally possible to determine certain minerals quantitatively and others semiquantitatively by chemical analysis. Prior to the chemical analysis the clay fraction, one should examine by all possible structural analysis techniques, such as, X-ray diffraction, infrared spectroscopy, electron microscopy, thermal analysis and electron diffraction. But by chemical analysis, one should taking into consideration of the effect of exchangeable ions, solvation with different liquids & thermal treatment.

3.5.2 Testing Samples

Five samples was taken into consideration by mixing samples from each layers of the soil fraction in order to obtain a sample which represent the mean characteristic of the soil layers except sample A_I which was taken from the location at Lumpini at the elevation between -1.40 m to -1.50 m.

Sample A_{II} was taken from the same location as A_I's at the elevation between -3.50 m to 5.90 m.

Sample B from Nong Ngu Hao taken at elevation -40 m to -7.0 m.

Sample C from Din Daeng taken at elevation -2.55 m to -11.0 m.

Sample D from Petchaburi Road, taken from elevation -2.0 m to -5.0 m.

All the sample tested, soil particles which are less than 2μ were taken into consideration. Anotherword, only clay fraction, was separated from the soil sample, which was experimented by this method.

3.5.3.1 Testing procedure ignitial weight loss was determined by heating the samples.

3.5.3.2 The sample was brought into solution by the introduction of hydrofluric acid, HF, associated with heat. Minerals in the solution were then decomposed in the form of oxides eg.. silicon oxide, aluminum oxide, ferric oxide etc.

3.5.3.3 From the solution obtained by the previous step, the contents of each element can be determined by the atomic absorption spectrophotometric and flame emission systems.