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### 1. Amorphous content

The amounts of mono-crystalline materials, even when small, can contribute significantly to the physical and chemical properties of soil, since they may have: -

High cation exchange capacity, which may be influenced by pH

High surface area

High reactivity with phosphate and organic

Therefore it is important to characterise and quantify the amount of non-crystalline materials present in soil as well as the amount of the crystalline components (American Society of Agronomy, 1986).

Method from the Geotechnical Research Centre, Montreal, Canada based on method by Segalen (1968) was adopted for this purpose. Basically, the method involves of removing and determining the amorphous content ( $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ ) by alternate acid and base washings of the soil. Eight times of acid and base washing have been applied to the soil. Five selected soils namely, MR1, GT1, NEA4, PEA3 and CEA3 have been used in this experiment. Each soil was carried out in duplicate to check the quality of the data.

0.5-g of soil (< 2mm) was weighed into plastic centrifuge tubes. The centrifuge tubes were used to minimise the lost of sample during the experiment. *Acid washing*: 40 ml of 8 M hydrochloric acid (HCl) was added and put on the mechanical shaker for 20 minutes. The tube was then centrifuged for 5-6 minutes and the supernatant was decanted into 100ml volumetric flask. About 40 ml of distilled water was then added into the tube and was shaken thoroughly. It was centrifuged for 5 minutes and the supernatant was decanted into the same volumetric flask from acid washing. Distilled water was added into the mark (volumetric flask), mixed well and about 50ml was poured into a small plastic bottle for analysis.

*Base washing*: 40ml of 0.5 M sodium hydroxide (NaOH) was placed in the centrifuge tube and placed in a steaming water bath for exactly 5 minutes. It was centrifuged immediately and the supernatant was decanted into a 100-ml plastic volumetric flask. The flask was made up to the mark using distilled water, mixed and 50 ml was poured into a small plastic bottle to complete one cycle of acid-base washing.

This acid-base washing cycle was then repeated 8 times and all the supernatants were analysed for Fe, Al and Si using Atomic Absorption Spectrometer (AAS). If only a quick removal is desired, 2-3 washings may be sufficient, but to determine the amounts present, the entire 8 washings should be completed. Acid washings were used to determine the iron and aluminium contents and base washings for silica and aluminium contents. Once the total contents of each washing have been determined the cumulative amounts of each ( $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ ) were calculated and then plotted as illustrated in Figure 3.19 below. It is important to note that the total amount of  $\text{Al}_2\text{O}_3$  was calculated from both the acid and base washing (first acid washing + first base washing), and so on for all 8 washings. It is also important to measure the silica content in first and second acid washings, and iron in first and second base washings to detect any carryover.

Figure 3.19, curve I shows the standard extraction or dissolution curves of amorphous materials after acid or base washing. The significant increase in extraction curves indicate the removal of amorphous material in the first 4 cycles of washing. This is because the amorphous material is removed very quickly while the crystalline

material dissolves at a slow steady rate. The amount of the amorphous material is determined by extrapolating the linear portion of the graph back to the y-axis. The intercept (P) gives the amorphous content of the soils. Meanwhile Figure 3.19, curve II shows the extraction and dissolution of crystalline material after the first washing. This indicates that there was no amorphous material in this type of soil.

The dissolution curves of amorphous iron oxide ( $\text{Fe}_2\text{O}_3$ ), silica oxide ( $\text{SiO}_2$ ) and aluminium oxide ( $\text{Al}_2\text{O}_3$ ) materials from the experiment on five selected samples (samples were chosen based on the physical suitability for use as liner in section 3.2) are presented in Figure 3.20(a), (b), and (c) respectively. The curves were plotted as a function of cumulative amorphous materials (in mg/g) against number of washing. Figure 3.20(a) and (c) for Fe and Al showed typical/standard dissolution curves as discussed earlier based on Segalen (1968), where the total dissolution of iron oxide (Fe) occurred after 3 to 4 of washings and aluminium oxide (Al) after 2 to 3 of washings. However, the dissolution curves in Figure 3.20(b) show that the amorphous silicon oxide (Si) was totally removed after five washings. It should be noted that the dissolution curves were linear after five washings. This clearly indicates that the silicon from crystalline materials was dissolved after five washings.

The result of the amorphous iron ( $\text{Fe}_2\text{O}_3$ ), silicon ( $\text{SiO}_2$ ), and aluminium oxides ( $\text{Al}_2\text{O}_3$ ) are presented in Table 3.13 for five selected samples. It can be concluded that estuarine samples from Newport (PEA3) contained the highest total amorphous material 13.4%. The lowest amorphous content was in sample estuarine alluvium from Cardiff (CEA3) which is about 8.5% only.

Figure 3.19. Typical dissolution curves obtained using the Segalen's method (after Segalen, 1968). (I) The dissolution of amorphous material. (II) The dissolution of crystalline material.

## **2. Organic content**

A method from the Laboratory Geotechnical Research Centre, Montreal, Canada was adopted to determine the percentage of organic content in soils. About 2 g of oven-dried soil was weighed into a dry pre-weighed 600ml beaker. A small amount (5-10 ml) of hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%) was added into the soil. The reaction in the

beaker was observed. It was then gently warmed on the sand-bath to speed up the reaction.

More H<sub>2</sub>O<sub>2</sub> was added when the reaction stopped. This adding process was undertaken periodically until no further reaction occurred. It was then permitted to settle overnight. On the next day, the state of reaction was checked by an addition of more H<sub>2</sub>O<sub>2</sub>. About 150 ml of distilled water was added and mixed into the solution when the reaction had completely stopped. The solution was left to stand overnight. The next morning, all the clear liquid was pipetted out from the beaker and the solid sample was then put into the oven to dry out. The beaker was then re-weighed. The percentage of the organic material in the soil was determine using the following equation:

$$\% \text{ Organic in soil} = \frac{(\text{Total weight before reaction} - \text{total weight after reaction}) \times 100}{(\text{Weight of soil})}$$

### **3. Specific surface area**

Surface area is determined by measuring the amount of a liquid or gas required to cover the surface of the soil (Yong and Warkentin, 1966). The method applied in this study was based on the weight of ethylene glycol adsorbed as monomolecular layer on the clay surface. The method for this test was adopted from the Laboratory Geotechnical Research Centre, Montreal, Canada. Organic free samples from section 1.0 above were used in this experiment. The sample (approximately 1.0g) was firstly weighed together with an aluminium-weighing dish and was then placed on the covered petri dish. The sample was then dried in an evacuated dessicator over silica gel and periodically (every hour) weighed until a constant weight was obtained. When this was reached, reagent grade ethylene glycol monoethyl ether (EGME) was added by pipette to cover the surface of the dried soil. It was then left to equilibrate for one hour.

The silica gel in the bottom of the dessicator was replaced with the CaCl<sub>2</sub>-EGME solvate. CaCl<sub>2</sub>-EGME was made by mixing 20g of EGME with 100g of hot oven

dried CaCl<sub>2</sub> into a 1L beaker and it was then allowed to cool down before spread it on the bottom of the dessicator. Sample-EGME slurry was placed in the petri dish and covered with a ventilated cover. The sample was then placed in the dessicator where it was evacuated with high vacuum pump for 45 minutes and left under vacuum for 1 hour prior to weighing. The process was repeated successively with longer time intervals until constant weight was reached. The calculation of the surface area is explained below:

It has been calculated that  $2.86 \times 10^{-4}$  g EGME is equal to monolayer of 1m<sup>2</sup> surface area. Then, the surface area (m<sup>2</sup>/g) of the soil was calculated as: -

$$\frac{\text{Weight of EGME retained (mg)}}{\text{Weight of dry soil (mg)}} \times \frac{(1\text{m}^2)}{(0.286 \text{ mg EGME})}$$

#### 4. Cation exchange capacity (CEC)

Cation exchange capacity (CEC) is the quantity of cations reversibly adsorbed per unit weight of mineral. The CEC was determined using batch tests with ammonium acetate exchange as described by ASTM D4319 (ASTM, 1984). Ammonium acetate solution was used as a buffer solution in this experiment where, the ammonium ion (NH<sub>4</sub><sup>+</sup>) will saturate the exchange complex and force the exchangeable ions into solution.

The quantity of exchangeable cations held is the cation exchange capacity, and is equal to the amount of negative charge. Exchangeable cations are the positive charged ions from salts in the pore water which are attracted to the surface of clay particles to balance the negative charge (Yong and Warkentin, 1966).

Preparation of ammonium acetate (1.0 N solution);

To 700 ml of distilled water (in a 1L-glass beaker), 57 ml of acetic acid and 68 ml of ammonium hydroxide were added and mix together. The solution in the beaker was then stirred using magnetic stirrer. The pH of the solution was adjusted to pH 7.0 by adding using droplet acid (acetic acid) or base (ammonium hydroxide). The solution was then transferred to a 1-L volumetric flask and top up to the mark with distilled water.

4 g of air-dried and pulverised soil was accurately weighed into a plastic centrifuge tube. 33 ml of ammonium acetate solution was added and was shaken in a mechanical shaker for 1 hour. Then, the tube was centrifuged and clear supernatant was decanted into 100ml volumetric flask. The procedures above were repeated twice on the same soil and all supernatants were placed into the same flask and top-up to the mark with distilled water. It was then analysed for cations using ICPAES.

Calculations: -

The cations in the flasks are extractable cations,

$$\text{Extractable cation (meq/100g)} = \frac{[\text{Concentration of cation in flask (meq/L)}] \times 10}{\text{Weight of soil (g)}}$$

The amount of exchangeable cation was determined by subtracting the soluble cation in the porewater from extractable cations.

$$\begin{array}{rcc} \text{Exchangeable cation} & = & \text{Extractable cation} \text{ -- } \text{Soluble cation} \\ \text{(meq/100 g)} & & \text{(meq/100 g)} \quad \text{(meq/100 g)} \end{array}$$

The soluble cations were determined from the saturation extract test (Section 3.3.3). These calculations were performed for each cation species as well as for total cations.

## 5. X-ray diffraction

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

### a. Sample preparation

The glass slide method was utilised in this study because of its ease of application (Figure 3.18). All of the sample preparation must be accomplished with a minimum of chemical and physical damage to the clay minerals present. The rule is to do as little as possible to the sample before presenting it to the x-ray beam. Organic-free

soils less than 63 $\mu\text{m}$  (after the organic test from Section 3.3.1) were used. According to Moore and Reynolds (1989), organic matter can produce broad x-ray diffraction peaks, and may increase the background, and inhibit dispersal of other minerals.

About 1g of soil was then placed into 10ml measuring cylinder. About 5ml of distilled water was then added in to it and was mixed thoroughly using a glass rod. After 15-20 minutes, the upper solution was then pipetted (using an eyedropper) and placed slowly on the clean glass slide so that the liquid covered the entire surface of the slide. A porous ceramic plate was used under the slide to catch any spills. It was assumed, according to Stoke's Law, that the solution that was sampled contained the clay particles of less than 2  $\mu\text{m}$ . The slide was dried at the room temperature. High drying temperature should not be used because poorly crystallised clay minerals in soils can be damaged by high temperature. Several treatments have been undertaken to verify the clay minerals in the soil. These treatments were: -

#### *Glycol treatment*

The sample was exposed to the vapour of the reagent ethylene glycol solvation. It was dried in the oven at 60°C and then re-analysed to determine the presence of montmorillonite. Montmorillonite is easily identified by comparing patterns of air-dried and ethylene glycol-solvated preparations. The glycol-treated preparations give a very strong 001 reflection at about  $5.2^{\circ}2\theta$  (16.9 Å), which, in the air-dried condition, shifts to about  $6^{\circ}$  (15 Å) (Moore and Reynolds, 1989).

#### *Heat treatment*

The slide was heated in the furnace at a temperature of 550°C for 30-40 minutes to verify the chlorite and kaolinite peaks. Heating chlorite to 550°C for 1 hour causes dehydroxylation of the hydroxide sheet with attendant changes in the diffraction pattern. The intensity of the 001 reflection increases greatly and shifts to about 6.3 to 6.4  $^{\circ}2\theta$ , and the 002, 003 and 004 reflections are much weakened. At this temperature, kaolinite becomes amorphous to X-rays and its diffraction pattern disappears. This test may suggest that chlorite is present or that chlorite is absent (Moore and Reynolds, 1989).

### *Hydrochloric acid treatment*

0.2g of organic-free soil sample was placed into the centrifuge tube. About 5ml of concentrated hydrochloric (HCl) was added and heated for 10-15 minutes. It was washed with distilled water for 3-4 times to neutralise the acid. The sample was centrifuged, the wash water was discarded and the soil left was oven dried and powdered. The sample was then used for preparation of another glass slide. This treatment was used to destroy the chlorite peaks and to distinguish chlorite from kaolinite.

### b. Qualitative analysis

The clay minerals were identified using the X-ray diffraction patterns (diffractogram) which by the peak's position, intensity, shape and breadth. Peak position is determined using Bragg's law which is written as  $n\lambda = 2d\sin \theta$ . Most of the important clay peaks are at the  $2\theta$  values of  $40^\circ$  or less; therefore,  $\theta$  is  $20^\circ$  or less. The identification of clay minerals was accomplished by careful consideration of peak positions and intensities. The qualitative identification procedure began by searching for a mineral that explains the strongest peak or peaks, then confirming the choice by finding the positions of weaker peaks for the same mineral. Once a set of peaks was confirmed as belonging to a mineral, these peaks were eliminated from consideration. From the remaining peaks, a mineral that will explain the strongest remaining peak or peaks was searched and then confirmed by looking for its peaks of lesser intensity. This method was repeated until all peaks were identified.

The determinations of clay minerals were based on the treatment results described earlier. Illite and glauconite profiles are unaffected by ethylene glycol solvation and heating to  $550^\circ\text{C}$ . Glauconite has a higher 001/003 intensity ratio than illite, but the main difference is the very weak or non-existent glauconite 002 reflection whose weakness is caused by heavy scattering from octahedral iron (Moore and Reynolds, 1989).

Chlorite has a basal series of diffraction peaks based on a first-order reflection of  $14.2 \text{ \AA}$ . Kaolinite has reflections based on a  $7.1 \text{ \AA}$  structure. Most kaolinites have the 002 peak at  $24.9^\circ 2\theta$ , and chlorite has its 004 reflection at  $25.1^\circ 2\theta$ . Positive identification



of chlorite is provided by peaks at 6.2 and 18.8<sup>0</sup>2θ, but these peaks are often weak and may not be detectable if the chlorite concentration is low. The chlorite and kaolinite can be differentiated by treated chemically or heated and then re-examined. Montmorillonite is easily identified by comparing diffraction patterns of air-dried and ethylene glycol-solvated preparations (Moore and Reynolds, 1989).

The results of the clay mineralogy based on the interpretation of X-ray diffraction are presented in Appendix D. The clay mineralogy of soil samples of MR, GT, NEA, PEA, CEA, and SGT were identified qualitatively based on the diffraction pattern. It is important to emphasise that the main purpose of the XRD study is only to identify the type of clay minerals in the soils. How much is present in these soils is beyond the scope of this study. However, for detail investigation of clay mineralogy, the quantity of clay minerals present is important.

## **6. Carbonate content determination**

The rapid titration method from Hesse (1972) was used to determine the carbonate content of all soils. This method is suitable for the routine analysis of a large number of samples where an accuracy of about 1.0% is sufficient (Hesse, 1972). 5g of 2mm-soil were placed into a 250cm<sup>3</sup> tall-form beaker. 100ml of 1.0M hydrochloric acid (HCl) were slowly added from a burette. The beaker was covered with speedy-vap clock glass and allowed to stand and stirred occasionally for 1 hour. After all the sediment had settled and clear liquid was obtained, 20 ml of the supernatant liquid was then pipetted into a conical flask with 6 drops of bromthymol blue indicator solution and titrated with 1M sodium hydroxide (NaOH). Duplicates of each soil were undertaken to check the quality of the result. The blank (without soil sample) was set-up by titration of 20 ml of original acid, HCl with 1M sodium hydroxide using bromthymol blue indicator.

Observation: - The bromthymol blue indicator showed the yellowish colour when added into the blank and soil solution. In blank, the yellowish colour changed to blue with addition of NaOH. Meanwhile in the soil solution, the colour changed from yellow to orange and with further addition of NaOH the colour changed to greenish.

Calculation:  $\%CaCO_3 = (\text{Blank titre} - \text{Actual titre}) \times 5$

The results of the carbonate content are summarised in Table 3.12 below. Table 3.12 clearly indicates that estuarine alluvium samples (NEA, PEA and CEA) have high percentage of carbonate compare to other samples MR, GT and SGT.