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Cation Exchange Capacity Of a Quartz-Rich Soil in an Acidic and Basic Environment

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Abstract. In this research, the time-dependent changes induced in charge characteristics of phosphoric acid and lime treated quartz-rich kaolinitic soil were investigated. Also, in order to study the relationship between the exchange capacity and the pore water chemistry, pH measurements was performed on cured samples. Based on the collected data, it was found that the pH of stabilized soils showed a tendency for reaching soil's natural pH with increasing curing time. In addition, the increase in number of broken bonds around the edges of soil particles and also the formation of cementitious compounds that acquired negative charges contributed to achieving higher CEC_p values at longer curing periods. From engineering point of view, the lime treated samples revealed the highest degree of improvement with an approximately 16-fold strength increase in comparison to the natural soil over an 8 months curing period.

Introduction

Clay minerals have the property of absorbing certain ions and retaining them in an exchangeable state. The most common exchangeable cations, in order of usual relative abundance, are Ca²⁺, Mg²⁺, H⁺, K⁺, NH₄⁺, Na⁺ [1]. The basal siloxane surfaces of kaolinite are believed by many researchers to carry a constant structural charge due to the isomorphous substitution of Si⁴⁺ by Al³⁺, whereas the charge on the edges is due to the protonation/deprotonation of exposed hydroxyl groups and therefore depends on the solution pH [2-4]. For instance, in the case of edge CEC, assuming A⁺ is the index cation, the following reactions take place [5]:

(1)

An increase in the [A⁺] concentration will push the exchange reaction towards the right and decrease Si-OH on the broken edges, giving rise to a higher CEC value. Therefore, under acidic conditions, the cation exchange sites on the edges of kaolinite crystals and other phyllosilicate plates can not simply be considered to be completely inactive. This paper aims to study the time-dependent changes induced in charge characteristics of a quartz-rich kaolinitic soil in an acidic and basic medium.

Research methodology

Materials. A pinkish tropical soil rich in quartz and kaolinite mineral was used in this investigation. It was excavated from a hillside (Balai Cerap) located in the skudai campus of Universiti Teknologi Malaysia. The physicochemical characteristics and the morphology of the natural soil are presented in Table and Fig 1, respectively.

Table 1 The engineering properties and chemical composition of the natural soil

Engineering & Physical Properties	Values	Chemical Composition (Oxides)	Values (%)
CEC [meq/100 g]	10.56	SiO ₂	39.77
pH [L/S = 2.5]	4.64	Al ₂ O ₃	32.88
Specific Gravity	2.73	P ₂ O ₅	4.83
Surface area [m ² /g]	20.63	K ₂ O	1.97
Liquid Limit, LL [%]	46.10	SO ₃	0.77
Plastic Limit, PL [%]	28.60	CuO	5.68
Plasticity Index, PI [%]	17.50	ZnO	2.16
BS Classification	ML	CO ₂	1.59
ICL [%]	3.00	Soluble Phosphorus (P)	3.50 ppm
Maximum dry density [Mg/m ³]	1.58	Soluble Aluminum (Al)	0.60 ppm
Optimum moisture content [%]	20.00	Soluble Silica (SiO ₂)	4.00 ppm
Unconfined compressive strength [kPa]	197.00	Soluble Calcium (Ca)	0.40 ppm
Loss of ignition [%]	0.40

Fig. 1 Morphology of natural soil

Sample preparation. According to the previous studies conducted regarding the stabilization of clayey soils [6-8], 5 and 3% phosphoric acid and lime by weight of the dry soil were chosen for this investigation. Samples were then compacted into a thin wall PVC tubes (50 mm diameter × 100 mm length) under constant compactive effort as specified in clause 4.1.5 of BS 1924: Part2 [9]. They were sealed to the atmosphere with rubber tight lids and stored in a room with constant temperature (27±2°C) until being tested at 1 month, 4 months, and 8 months curing period [10].

Laboratory investigation. The CEC_p is defined as the cation exchange capacity (CEC) attributed to the permanent charges of the clay structure. The methods of measurement are usually based on determining the quantity of a particular exchangeable cation by chemical and spectroscopic means and expressing the result per 100 g of the dry soil. Although, no general method exist that can be reliably used to determine the CEC value. However, the use of divalent Barium (Ba²⁺) as a saturating cation is considered to be more effective, especially in determining the CEC for kaolinite minerals [11]. In this paper, the revised version suggested by Tan and Dowling [12] was used for

CEC_p measurements. In order to determine the CEC_p caused by permanent charges, it was necessary to block the variable exchange sites. This was achieved by acidifying the soil so that the cations on the variable sites were replaced by protons. Hence, 10 g of the soil were placed into a 100 mL polyethylene centrifuge tube. Next, 30 mL of 0.1M HCL was added, and the bottle was shaken for 15 min with a mechanical shaker. Then, the sample was centrifuged at 6,000 rpm for 20 min, and the supernatant was discarded very carefully to avoid loss of solids. To the acidified soil 50 mL of 0.3M BaCl₂ solution was added. The mixture was shaken for 30 min with a mechanical shaker and the supernatant was discarded from the centrifuged sample. After the clay material had been saturated with Ba²⁺ ions, the sample was washed two times with 50 mL of distilled water to remove non-exchanged Ba²⁺ ions. In the next step called the extraction step, after the addition of 50 mL of 0.3M CaCl₂ solution to the washed Ba-saturated soil, the sample was shaken for 30 min, centrifuged, and the supernatant was collected carefully into a 100 mL volumetric flask. The washing step was performed one more time with 30 mL of distilled water. The centrifuged wash water was added to the solution in the volumetric flask. Finally, the extracted solution was analyzed for Ba concentration using an ICP spectrometer, and the CEC_p value (mEq/100g) for each sample was determined from the results.

A Hannah model HI 8424 pH meter was used to measure the pH value of treated samples. The data were obtained in triplicate, and the average pH was reported. Also for convenience, in conjunction with the pH electrodes, an automatic temperature compensation probe was employed to correct pH readings to the equivalent pH at 25°C.

In this research, unconfined compressive strength test (UCS) was carried out in order to determine the degree of improvement in the treated samples, with at least three specimens being tested for each mix design. Hence, after reaching the specified curing time, samples were taken from thin wall PVC tubes and directly tested at an axial strain rate of one percent per minute.

Results and discussion

Figure 2 shows the changes in pH value of lime and phosphoric acid treated pink soil samples with curing time. As was expected, the acid treatment reduced the pH of the solution to a greater intensity. The latter was due to the acidic nature of the untreated soil (pH=4.64). It was also clear that as the amount of stabilizer increased, the variation in pH value were more significant implying that the stabilizer content was predominantly controlling the pore water chemistry.

CEC_p value for untreated and 5% lime and phosphoric acid treated soil are shown in Fig 3. As can be seen, the lime treatment caused a sharp increase in the CEC_p value after 1 month of curing. This was probably due to an increase in the number of negatively charged surface hydroxyl groups and also the formation of new products. At 4 months time interval, a reduction in the CEC_p values of both mix designs was observed. However, with increasing curing time to 8 months, the CEC_p value of chemically treated samples increased. The latter was probably due to a rise in the number of broken bonds around the edges of particles and also the formation of cementitious compounds that acquired negative charges in the soil-stabilizer matrix.

In Fig 4, the unconfined compressive strength of untreated and soil treated with 3 and 5% phosphoric acid and lime are presented. As can be seen, cylindrical specimens of 5% acid treated (AT) samples attained an unconfined compressive strength of 1509 kPa, over 8 months curing period. On the other hand, it was clear that the strengths of lime treated (LT) samples were much higher than acid mix designs. For instance, at 5% lime content, the strengths reached a value of 3155 kPa after 8 months of curing. This indicated an increase of approximately 16-fold in comparison to the strength of natural soil (Table 1). It worth to note that, in comparison to the early stages of curing, increasing curing time from 1 to 8 months resulted in a much lower gain in the compressive strength of all lime mix designs. This was probably due to the rapid consumption of calcium ions in the soil-lime reactions. Whereas, the longer term strength development for acid treated samples was likely to be more reliant upon the slow weathering action of acid on the soil structure and the subsequent formation of reaction products.

Fig. 2 Variation of pH for soil mix designs

Fig. 3 Time-dependent changes in CEC_p of pink Soil samples

Fig. 4 Strength development for Pink Soil (PS) mix designs

Conclusions

This research was carried out in an attempt to study the behavior of soil exchange sites under acidic and basic conditions. The acidic nature of untreated sample was confirmed with the low pH value obtained for this soil. From the results, it was also clear that with the progression of time, the pH value showed a tendency for reaching its natural state. This was due to the formation of new products and the subsequent exhaustion of alkaline and acid ions in the pore water.

Cation exchange capacity caused by permanent charges (CEC_p) was also studied for design mixes that showed the highest degree of improvement. The results emphasized on the fact that the charge developments on the surface of soil particles were highly dependent on the ions present in the pore water. Also it was found that the CEC results were consistent with the compressive

strength data obtained for lime mix designs. This was due to the formation of cementitious compounds that acquired negative charges and hence contributed to higher CEC values.

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