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TECHNICAL NOTE

Cation Exchange Capacity of Phosphoric Acid and Lime Stabilized Montmorillonitic and Kaolinitic Soils

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Abstract Studies on the chemically stabilized soils have shown that the effectiveness of treatment is largely dependent on soil's natural environment. In this research, the time-dependent changes induced in permanent cation exchange capacity of lime and phosphoric acid treated soils, comprised mainly of montmorillonite and kaolinite minerals, were investigated. Also, in order to study the relationship between the exchange capacity and acidity/alkalinity of pore water, pH measurements were 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. Nevertheless, the kaolinite mineral with pH-dependent structural properties, showed a rather limited behavior in the acidic medium. From engineering point of view, the lime treated samples revealed the highest degree of improvement with an approximately ten-fold strength increase in comparison to the natural soil over an 8 months curing period.

Keywords Bentonite · Kaolinite · Stabilization · Phosphoric acid · Lime · Cation exchange capacity · pH

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1 Introduction

Under a given set of environmental conditions (temperature, pressure, pH, and chemical composition of water), clay minerals can adsorb cations of specific types and amounts (Mitchell and Soga 2005). This is a surface phenomenon and usually occurs in response to the electric charge carried by the clay particles. In general, there are two major sources of charges on clay lattice:

(a) The pH-dependent charges that is associated primarily with the hydroxyl groups attached to silicon and aluminum on the surfaces and edges of the clay minerals (Mathew and Narasimha 1997). This is believed to be the major source of charge in kaolinite minerals. In kaolinite, the proton is presented as OH groups on the surface planes of the mineral. Hence, if the clay mineral is exposed to a high pH environment, the

hydrogen dissociates from the OH group, leading to a negative charge on the clay surface. Exposed hydroxyl groups are also present in the sesqui-oxides, amorphous, and para-crystalline clays.

(b) The negative charges induced by the isomorphic substitution of ions within the clay lattice. These charges are permanent feature of the mineral crystal and do not depend upon the chemical composition of the ambient solution. For instance, the OH groups in the smectite clays are not present as exposed OH groups. They are contained within the crystal, covered by layers of silica tetrahedrons. Therefore, smectite has its negative charge mainly from isomorphous substitution.

The negative charges are usually neutralized by a swarm of positively charged ions (cations). These cations, which are held electrostatically on the surface of the soil colloids, are called adsorbed cations. The cation exchange capacity, frequently abbreviated as CEC, is a quantitative measure of all the cations adsorbed on the surface of the soil colloids. The amount is usually expressed in milliequivalent (mEq) per 100 g of soils. Because of differences in concepts, and in view of the presence of permanent and variable charges contributing to cation exchange reactions, several types of CEC have currently been identified. The most important of these types are:

(a) CEC_p, which is the CEC produced by the permanent negative charges of the clay minerals.
(b) CEC_v, which is the CEC resulting from the pH dependent (or variable) charges of the inorganic and organic colloids.
(c) CEC_t, which is the total CEC caused by both the permanent and variable charges of the soil colloids.

Depending on mineralogy, temperate mineral soils are likely to have measurable CEC_t at any pH due to the presence of CEC_p on 2:1 clay minerals, with additional CEC_v determined primarily by the amount of soil organic matter present. In addition, the presence of hydrous oxides of Fe and Al in highly weathered tropical soils may result in a net positive charge and the dominance of anion exchange in these soils at low pH environment (Ross 1989).

This paper aims to identify the main exchange reactions that contribute to the stabilization process of montmorillonite and kaolinite dominated soils treated with two different type of stabilizers, i.e., lime (alkaline stabilizer) and phosphoric acid (acidic stabilizer). Hence, the changes induced in the charge characteristics of the exchange sites were monitored at different time intervals.

2 Research Methodology

2.1 Materials

Based on the structural properties and environmental conditions, two types of clay minerals were selected for this investigation. First of all, the more expansive and pure bentonite soil comprised mainly of sodium-montmorillonite mineral was used in this investigation. Sodium montmorillonite has a high swelling capacity and forms gel-like masses when added to water (Grim and Guven 1978). The soil is an odorless, dry, greenish powder sold under the name of "Quick Gel". The Second type of soil was a white and odorless kaolin powder. It should be noted that the minerals present in these two soil types (montmorillonite and kaolinite) represent the opposite extremes of structural charge developments, hence they can serve as index for predicting the behavior of other clay minerals which exhibit intermediate behaviors (Ingles and Metcalf 1972). The engineering properties and chemical composition of the natural soils used in this investigation are presented in Table 1. It should be noted that the chemical composition of lime and phosphoric acid (Merck, 85 % H_3PO_4) used in this research are shown in Tables 2 and 3, respectively.

2.2 Sample Preparation

Clause 3.3.4.1 of BS 1377: Part 4 (1990a) was adopted in order to determine the optimum moisture content of the different design mixes. Also according to the previous studies conducted regarding the stabilization of clayey soils (Medina and Guida 1995; Bell 1996; Rogers et al. 1996), different amounts of phosphoric acid and lime, were chosen for each individual soil. 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 (1990b). They were sealed to the atmosphere with rubber tight lids and stored in a

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

Physical properties	Values		Chemical composition (oxides)	Values (%)	
	GB[*]	WK[*]		GB	WK
CEC (meq/100 g)	78.79	12.87	SiO_2	60.79	48.18
pH (L/S = 2.5)	9.03	4.34	Al_2O_3	21.20	31.10
Liquid limit, LL (%)	301.60	42.20	Fe_2O_3	6.46	1.03
Plastic limit, PL (%)	41.80	21.30	CaO	0.96	(–)[*]
Plasticity index, PI (%)	259.80	20.90	MgO	3.26	0.86
BS classification	CE	CL	Na_2O	6.14	(–)
ICL (%)	7.0	2.0	CO_2	1.19	1.34
Maximum dry density (Mg/m^3)	1.27	1.64	P_2O_5	(–)	9.37
Optimum moisture content (%)	37.70	18.40	K_2O	(–)	4.01
UCS[*] (kPa)	281.30	134	SO_3	(–)	2.07

[*]*GB* Green Bentonite, *WK* White Kaolin, *UCS* Unconfined Compressive Strength, (–) not detected

Table 2 Chemical composition of the hydrated lime

Chemical composition	Values (%)
Calcium Oxide, CaO	74.23
Phosphorus Oxide, P_2O_5	0.08
Magnesium Oxide, MgO	0.74
Calcium Sulphate, $CaSO_4$	0.12
Ferric Oxide, Fe_2O_3	0.17
Aluminium Oxide, Al_2O_3	0.11
Silica, SiO_2	0.14
Loss on Ignition, LOI	24.35

Table 3 Chemical composition of the phosphoric acid

Chemical composition	Maximum quantity (ppm)
Chloride (cl)	2.0
Fluoride (F)	1.0
Nitrate (NO_3)	3.0
Sulphate (SO_4)	20.0
Calcium (Ca)	20.0
Copper (Cu)	0.5
Potassium (K)	5.0
Magnesium (Mg)	5.0
Sodium (Na)	200.0
Zinc (Zn)	2.0
Lead (Pb)	0.5
Insoluble matter	10.0

room with constant temperature (27 ± 2 °C) until being tested at 1, 4 and 8 months curing period (Eisazadeh 2010). In addition, for more convenience in the presentation of the results, a specimen designation scheme was implemented. Letters in the specimen designation indicated soil name, type, and amount of stabilizer (by weight of the dry soil) used respectively (i.e., GB: Green Bentonite, WK: White Kaolin, AT: Acid Treated, LT: Lime Treated).

2.3 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 (Ba^{2+}) as a saturating cation is considered to be more effective, especially in determining the CEC for kaolinite minerals (Tan 2005). In this paper, the revised version suggested by Tan and Dowling (1984) 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 0.1 M 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 0.3 M BaCl$_2$ 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 Ba^{2+} ions, the sample was washed two times with 50 mL of distilled water to remove non-exchanged Ba^{2+} ions. In the next step called the extraction step, after the addition of 50 mL of 0.3 M CaCl$_2$ 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 centri-fuged wash water was added to the solution in the volumetric flask. Finally, the extracted solution was analyzed for Ba concentration using an ICP spectrom-eter, and the CEC$_p$ value (mEq/100 g) for each sample was determined from the results.

The pH of soil solution provides useful information regarding soil-chemical reactions as it reflects the changes occurring in the medium. In this study, a Hannah model HI 8424 pH meter was used to measure the pH value of treated samples according to BS 1377: Part 3 (1990). The data were obtained in triplicate, and the average pH was reported. In addition, three com-mercially available pH buffers (pH 4, pH 7, and pH 9.2) were used to calibrate the instrument prior to each measurement. Also for convenience, in conjunction with the pH electrodes, an automatic temperature compensa-tion probe was employed to correct pH readings to the equivalent pH at 25 °C. After conducting the test, all electrodes were cleaned according to the manufacturer's instructions. However, after use in bentonite samples, it was necessary to stand the electrode in a strong detergent to remove residue and to keep the electrode within the required operating parameters.

In this research, unconfined compressive strength (UCS) test was carried out in accordance with BS 1924: Part 2 (1990b), 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 1 % per minute.

3 Results and Discussion

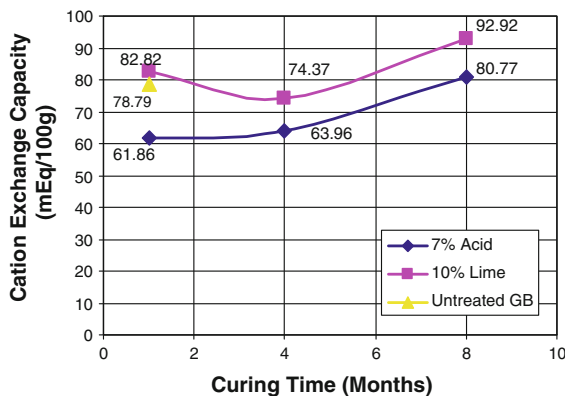In Figs. 1 and 2, the pH values for Green Bentonite and White Kaolin samples are shown. As can be seen, in
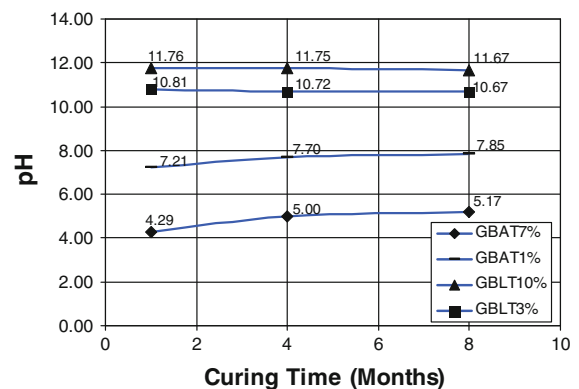
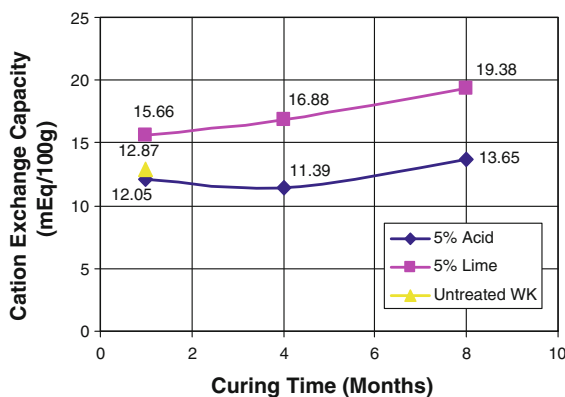**Fig. 1** Variation of pH for *Green* Bentonite mix designs
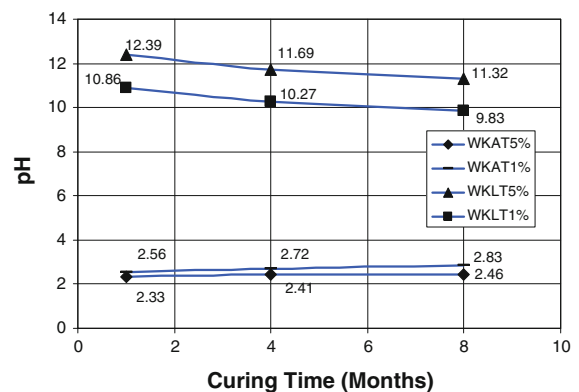
Fig. 2 Variation of pH for *White* Kaolin mix designs

phosphoric acid and lime mix designs, a reduction and a rise in the pH of soil solution were apparent, respectively. Moreover, the acid and lime treated samples with respect to Green Bentonite and White Kaolin soil types, revealed noticeable changes in the first 4 months curing period. This was expected due to the alkaline and acidic nature of the natural soils (Table 1). It was also clear that as the amount of stabilizer and curing time increased the variation in pH value were more significant implying that the stabilizer content was predominantly controlling the pore water chemistry. Furthermore, the addition of stabilizers caused wider changes in the pH value of chemically treated kaolin samples in comparison to bentonite soil. The importance of a broader pH variation was due to the presence of pH-dependent alumina and hydroxyl groups on the surface of kaolinite particles and the fact that at a high or low pH the clay edges acquired negative or positive charged sites attracting cations and anions, respectively.
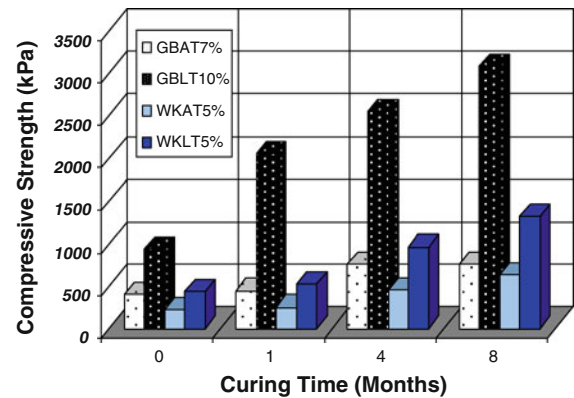
It was evident from the graphs presented in Fig. 3 and 4 that at the early stages of curing, in contrast to lime stabilized soils, acid treatment caused a significant decline in the CEC_p value of the material. This could be explained by the decrease in the pH value of the medium and also the subsequent protonation of the clay minerals which limited the accessibility to the exchange sites. Furthermore, in lime stabilized soil due to the increase in OH^- ion concentration of pore water and also the number of surface hydroxyls which lost H^+ ion and became negatively charged, an increase in the CEC_p value was observed (Ma and Eggleton 1999). Nevertheless, at 4 months curing period, a drop in the CEC_p value of lime treated bentonite samples was apparent. This was probably caused by a reduction in the OH^- ion concentration of

Fig. 5 Strength development for *Green* Bentonite and *White* Kaolin mix designs

pore water which resulted in development of less negative charges on the surface of clay particles (Grim 1968). On the other hand, with further curing, the increase in number of broken bonds around the edges of particles in the soil-stabilizer matrix and moreover the formation of cementitious compounds that acquired negative charges contributed to the CEC_p of the material, thus increasing the CEC_p value at 8 months curing period. On the other hand, the CEC_p value of phosphoric acid treated White Kaolin samples did not reveal a significant change with increasing curing time.

Figure 5 shows the UCS of phosphoric acid and lime treated samples under different stabilizer content and curing time conditions. As can be seen, the lime stabilization technique revealed the most promising results by achieving the highest degree of improvement after 8 months of curing, i.e., an increase of approximately 11.4 and 10 times with respect to the strength of natural Green Bentonite and White Kaolin soil (Table 1).

Fig. 3 Time-dependent changes in CEC_p of *Green* Bentonite samples

Fig. 4 Time-dependent changes in CEC_p of *White* Kaolin samples

4 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 White Kaolin samples was confirmed with the low pH value obtained for this soil. In contrast, an average pH value of 9.03 (alkaline) was obtained for the untreated bentonite soil. From the results, it was found that the

differences in pH value of treated samples due to the type of treatment were significant. It was also clear that as the amount of stabilizer ions had a profound impact on the pH of pore water. Furthermore, with the progression of time, the pH value in soil-stabilizer matrix showed a tendency for reaching its natural state due to formation of new products (Narasimha and Rajasekaran 1996) and the subsequent reduction of alkaline and acid ions in the pore water.

Cation exchange capacity caused by permanent charges (CEC_p) was 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 exposed hydroxyl groups had a noticeable impact on the overall CEC_p value of kaolinite mineral. On the other hand, the protonation of soil structure and also the amphoteric nature of clay alumina which ionizes positively in a low pH environment gave rise to a lower CEC_p values in the acid treated samples. Also it was found that in soil types comprised mainly of kaolinite mineral, in comparison to lime treatment, the changes in CEC_p value of acid treated samples were rather limited. This was because of the dependency of charges on the surface of clay particles to the pH of pore water which remained quite low for all curing periods. The CEC results were also consistent with the compressive strength data obtained for various mix designs which revealed a higher strength development for time dependent soil–lime reactions.

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