

2012

Stabilization of tropical kaolin soil with phosphoric acid and lime

Amin Eisazadeh, *University Technology Malaysia*

Khairul Anuar Kassim, *University Technology Malaysia*

Hadi Nur, *University Technology Malaysia*

Stabilization of tropical kaolin soil with phosphoric acid and lime

Amin Eisazadeh · Khairul Anuar Kassim · Hadi Nur

Received: 3 September 2009 / Accepted: 10 August 2011 / Published online: 20 August 2011
© Springer Science+Business Media B.V. 2011

Abstract Studies on the chemically stabilized soils have shown that the effectiveness of treatment is largely dependent on soil's natural environment. In tropical kaolin soils, phosphoric acid may be used as an alternative to traditional alkaline stabilizers for improving soil properties. This research was carried out in an effort to identify the time-dependent soil-stabilizer reactions. Data for the study of characterization of treated samples were obtained from X-ray diffractometry, energy dispersive X-ray spectrometry, field emission scanning electron microscopy, Fourier transform infrared spectroscopy, and leaching analysis. Based on the collected data, the kaolinite mineral with pH-dependent structural properties showed slightly different behavior both in basic and in acidic mediums. Also, it was found that the chemical stabilizers preferentially attacked the alumina surface of the clay particles. Therefore, it was rational to suggest that with respect to lime and phosphoric acid treatment, aluminate hydrate compounds are more likely to be formed.

Keywords Tropical kaolin · Stabilization · Phosphoric acid · Lime · Characterization · Leaching

1 Introduction

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Among these, kaolinitic clays are geochemically and industrially very versatile (Manju et al. 2001). These minerals are formed under tropical weathering conditions in areas where precipitation is relatively high, and there is good drainage to ensure leaching of cations and iron from acidic granitic rocks (Mitchell and Soga 2005). Soft kaolin

A. Eisazadeh (✉) · K. A. Kassim
Department of Geotechnic and Transportation, Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia
e-mail: A.Eisazadeh@yahoo.com

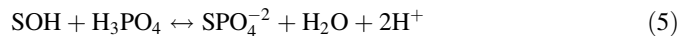
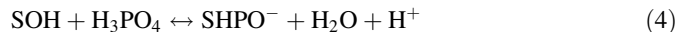
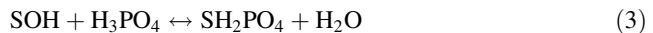
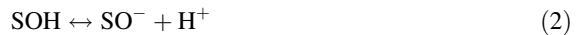
H. Nur
Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia,
81310 UTM Skudai, Johor, Malaysia

deposits are considered to have particularly poor engineering characteristics, exhibiting expansive properties, high plasticity, poor workability, and low shear strength. Therefore, the construction of structures on these deposits is confronted with many geotechnical problems. In such problematic clays, chemical stabilization techniques have proven to be effective (Ingles and Metcalf 1972).

The effect of calcium-based stabilizers on the geotechnical properties of soil has been examined by many investigators, and rational application guidelines and laboratory testing methods have been developed (Balasubramaniam et al. 1989; Locat et al. 1996; Bell 1996; Narasimha Rao and Rajasekaran 1996). However, the effectiveness of technique has been difficult to predict when applied to sulfate-rich soils (Mitchell and Dermatas 1992; Kota et al. 1996; Rogers et al. 1996; Rollings et al. 1999).

In general, acids are effective in removing alumina and other metallic oxides from clay minerals (Herzog and Mitchell 1963). Treatment of kaolinitic clays using phosphoric acid has been reported to bring several beneficial changes such as improved strength and workability (Lyons and McEwan 1962; Medina and Guida 1995). Furthermore, in addition to being cheaper to transport than traditional bulk stabilizer materials, the nontoxic nature of phosphoric acid is also a favorable feature, making them a potentially attractive alternative for treating acidic tropical soils.

The following equations can be given as the surface reactions of phosphate ion with kaolinite (Ioannou and Dimirkou 1997):



where SOH represents the surface functional group of kaolinite. Although all the exact mechanisms have not been identified, phosphate ions are known to react with iron and aluminum mineral surfaces in several different ways. For instance, the phosphate anions can be attracted to the surfaces of metallic oxides and the broken edges of kaolinite and form phosphorus containing compounds (Brady and Weil 1996). This is due to the fact that alumina which is exposed at the edges of kaolinite is amphoteric and ionizes positively at low pH environment. As a result, positive diffuse layers can develop at the edges of particles in an acid environment, promoting positive edge to negative surface interaction (Mitchell and Soga 2005).

The primary objective of this research was to evaluate the efficacy of phosphoric acid as a stabilizer in comparison with lime treatment and also to examine and suggest the relevant processes responsible for the physicochemical changes induced on the structure of tropical kaolin soils at different pH conditions.

2 Materials and experimental program

2.1 Materials

The bulk kaolin soil used in this investigation was a white, odorless, dry powder. The physical properties of the natural soil along with its chemical composition are presented in

Table 1 Physicochemical properties of natural kaolin soil

Engineering and physical properties	Values	Chemical composition (oxides)	Values (%)
CEC (meq/100 g)	12.87	SiO ₂	48.18
pH (L/S = 2.5)	4.34	Al ₂ O ₃	31.10
Specific gravity	2.66	Fe ₂ O ₃	1.03
External surface area (m ² /g)	19.87	MgO	0.86
Liquid limit, LL (%)	42.20	P ₂ O ₅	9.37
Plastic limit, PL (%)	21.30	K ₂ O	4.01
Plasticity index, PI (%)	20.90	SO ₃	2.07
IS classification	CL	CO ₂	1.34
ICL (%)	2	Soluble phosphorus (P)	5.10 ppm
Maximum dry density (Mg/m ³)	1.64	Soluble aluminum (Al)	5.80 ppm
Optimum moisture content (%)	18.40	Soluble silica (SiO ₂)	4.00 ppm
Unconfined compressive strength (kPa)	134	Soluble calcium (Ca)	0.40 ppm

Table 1. It should be mentioned that the lime used in this investigation was a laboratory-grade hydrated lime. In addition, the phosphoric acid was a Merck-analyzed, 85% H₃PO₄, of specific gravity 1.71.

2.2 Preparation of specimens

Clause 3.3.4.1 of BS 1377: Part 4: 1990 was adopted in order to determine the optimum moisture content of the natural soil. This moisture content was used in all mix designs, so that the changes observed in behavior of treated samples were solely due to the stabilizer action and not from the effects of varying water contents. Also, according to the previous studies conducted regarding the stabilization of kaolinitic soils (Medina and Guida 1995; Bell 1996), two different amounts of phosphoric acid and lime, i.e., 2 and 5% by weight of the dry soil, were selected for this research. Samples were then compacted into a 50-mm-diameter thin wall PVC tubes under constant compactive effort as specified in clause 4.1.5 of BS 1924: Part 2: 1990. They were sealed to the atmosphere with rubber tight lids and stored in a room with constant temperature ($27 \pm 2^\circ\text{C}$) until being tested at 1-, 4-, and 8-month curing period.

2.3 Testing program

In this research, the stabilized soil was characterized prior to and after treatment. The method and equipments used in each of these analyses are described as follows.

Leaching was performed based on a procedure slightly modified from the Environmental society of Canada (EC 1990), known as equilibrium extraction (EE) test. This test is based on achieving steady state conditions by stirring the treated material with distilled water and monitoring the pH changes until it reaches a constant value (Eisazadeh 2010). For each test, 20 g of solid particles was mixed with 160 mL of distilled water using a magnetic stirrer for 24 h. Then, after filtration, pH was measured, and the supernatant was preserved for ICP analysis of Si, Al, P, and Ca elements.

Powder X-ray diffraction (XRD) patterns for treated samples were measured with a Bruker D8 advance diffractometer using CuK α radiation ($\lambda = 1.54 \text{ \AA}$) and recording (2θ)

angles ranging from 6° to 90° . The mineralogical analysis was carried out based on the characteristic Bragg data available in the standard Powder Diffraction File (JCPDS 1995).

The morphological features and changes in the Al/Si, Ca/Si, and P/Si ratios of treated samples were monitored at different time intervals. Each sample was sputtered with platinum for 120 s at 30 mA under high vacuum conditions until they were completely coated. The samples were then examined using a JSM-6701F JEOL field emission scanning electron microscope (FESEM) equipped with energy-dispersive X-ray spectrometer (EDAX). The EDAX feature of the FESEM system allowed the detection and quantitative analysis of the major elements present on the surface of soil particles.

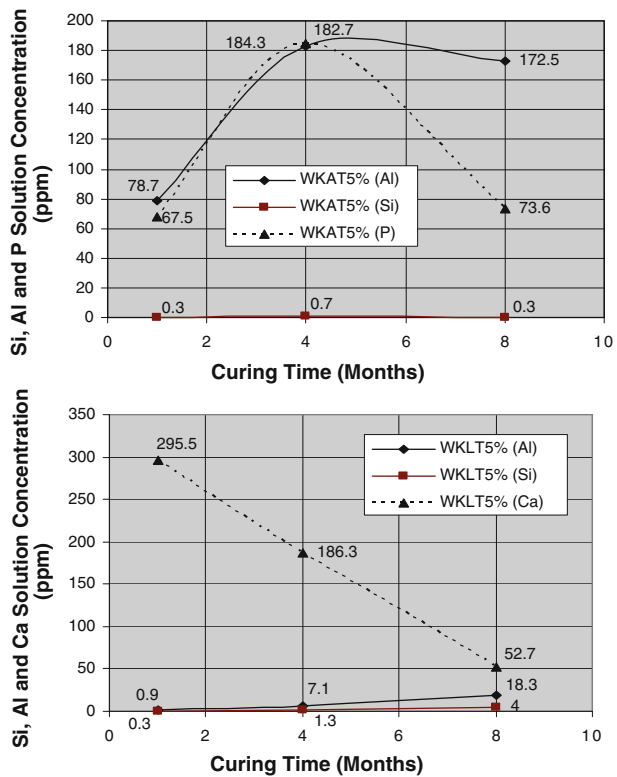
Fourier transform infrared spectroscopy (FTIR) was employed in order to study the molecular changes in the structure of treated soil. The analysis was conducted on a Perkin Elmer Spectrum 2000 instrument using KBr pellets. Hence, the transparent KBr disks were inserted in the instrument and analyzed with adsorption bands measured at characteristic wave numbers between 400 and $4,000\text{ cm}^{-1}$.

Unconfined compressive strength (UCS) test was performed on cured specimens at an axial strain rate of one percent per minute in accordance with BS 1924: Part 2: 1990. The results were used as an index of improvement. At the end of each test, the failed soil specimen was dried and weighed to determine its moisture content.

3 Results and discussion

The release of soluble Al, Si, P, or Ca from phosphoric acid- and lime-treated white kaolin samples at different time intervals is shown in Fig. 1, respectively. As seen in the lime-stabilized soil, with increasing curing time, there was a sharp reduction in the level of Ca monitored in the aqueous solution. This was consistent with the incorporation of Ca ion into the reaction products. On the other hand, the 5% phosphoric acid treated-samples released a soluble P concentration of 67.5 ppm at 1-month curing period while reaching an optimum of approximately 184 ppm after 4 months. This behavior confirmed the formation of inner-sphere complexes between the phosphate ion and the surface hydroxyl groups at the early stages of curing. Also, due to the amphoteric nature of alumina, positive-charged sites were developed at the edges of kaolinite minerals, thus attracting P ions to these sites. With further curing to 4 months, an increase in the level of soluble P was observed. This was caused by the weathering action of acid on the soil structure. It should be noted that the reduction in the level of soluble P at longer curing periods was consistent with the formation of new reaction products, which rendered them less soluble. According to the soluble Al data from both plots, the acid treatment caused much higher release of Al than the lime-treated samples while virtually reaching a constant value after 4-month curing period. This could be explained through the time-dependent weathering action of phosphoric acid and the higher solubility of Al ions in a low-pH environment (Brady and Weil 1996). On the other hand, for all mix designs, little soluble Si concentrations were observed. The reason responsible for this type of behavior was the fact that the hydroxyl groups exposed at the surface of kaolinite particles were strongly pH sensitive. Therefore, at high pH, there was a greater tendency for H^+ from the hydroxyls to go into the solution. This tendency in turn initiated mineral dissolution directly next to a source of alumina in the clay structure. On the other hand, at low pH, since the hydroxyl sites became positively charged, the clay alumina was released from surface sites by protonation action. It worth noting that a similar trend in Si, Al, and Ca release of lime-stabilized kaolin soils has been reported by Boardman et al. (2001).

Fig. 1 Levels of soluble Al, Si, P, or Ca release into the aqueous solution with respect to phosphoric acid and lime treatment



XRD graphs of natural, lime-, and phosphoric acid-treated soil are presented in Fig. 2. As shown, kaolinite mineral was identified by its strong diffraction lines at 12.5° and 25° 2θ angles (Brown 1961). The peaks observed at approximately 9° and 18° corresponded to illite and gibbsite, respectively. Other reflections at approximately 21° and 27° implied the presence of quartz mineral. On the other hand, for stabilized soils, all intensities of clay mineral reflections decreased with time. This was consistent with the vigorous action of acid on the clay structure and also the highly pozzolanic behavior of kaolinite in an alkaline environment. Furthermore, in lime-treated samples, a new reflection attributed to the formation of new reaction products was observed at 11.74° 2θ angle. The peak was tentatively assigned to calcium aluminate hydrate (CAH) compound (JCPDS 1995).

In this paper, EDAX was conducted in order to identify the elements present on the surface of clay particles. Also, the intensity of peaks at various time intervals was used to determine the relative changes induced by the chemical treatment on the soil structure. EDAX spectra for untreated, lime-, and phosphoric acid-treated samples along with their corresponding Al/Si, Ca/Si, and P/Si ratios are presented in Table 2 and Fig. 3a, b, c, respectively. In the spectrum, high intensities of aluminum (Al), silicon (Si), and phosphorus (P) followed by lower levels of iron (Fe), magnesium (Mg), sulfur (S), and potassium (K) were evident. Presence of these elements along with their intensity was in good agreement with kaolinite minerals' chemical composition (Carroll and Starkey 1971). As shown in Table 2, there were considerable changes in the Al/Si ratio of the stabilized samples. The increase in the Al/Si ratio of the treated samples after 4 months of curing time is consistent with a mechanism in which compounds of aluminate hydrate gels are

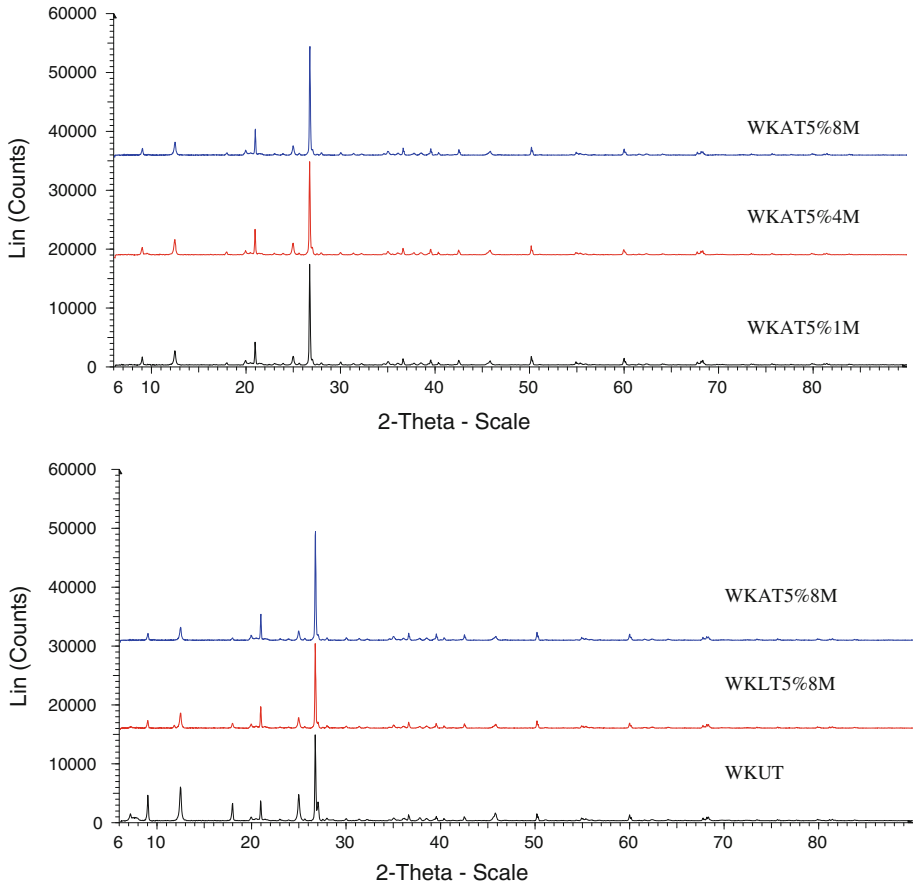


Fig. 2 X-ray diffraction patterns for untreated, lime- and phosphoric acid-treated kaolin soil at different time intervals

Table 2 Variation of Al/Si, Ca/Si, and P/Si ratios of various mix designs with curing time

Sample description		Ratio (wt%)		
Mix design	Curing time (months)	Al/Si	Ca/Si	P/Si
WKUT	–	0.63	0.00	0.19
WKAT5%	1	0.77	0.00	0.52
WKL5%	1	0.70	0.21	0.17
WKAT5%	4	0.84	0.00	0.47
WKL5%	4	0.75	0.20	0.11
WKAT5%	8	0.70	0.00	0.20
WKL5%	8	0.55	0.07	0.20

WK white kaolin, LT lime-treated, AT acid-treated, UT untreated

deposited on the surface of clay particles. On the other hand, after 8 months of curing, the Al/Si ratio showed a relatively lower value. This was because of an increase in the sources of silica present at the surface of 1:1 silica/alumina-structured kaolinite particles. This was

also believed to be the main cause of decrease in the Ca/Si and P/Si ratios of treated samples with curing time.

FESEM images for untreated, lime-, and phosphoric acid-treated white kaolin soil are presented in Fig. 4a, b, c, respectively. As shown, the neatly arranged book-like kaolinite particles are the predominant feature of the natural soil (Mitchell and Soga 2005). Comparison of the results indicated that the morphological changes seen in lime mix designs were similar to those observed in phosphoric acid-treated samples but with a lesser intensity. In addition, in both mix designs, after 8 months of curing, the formation of white cementitious compounds on the surfaces of soil particles was apparent (Willoughby et al. 1968; Rajasekaran and Narasimha Rao 1997).

The FTIR spectra of natural and chemically treated white kaolin soil are shown in Fig. 5. As can be seen, kaolinite was characterized by two strong bands at 3,696 and 3,620 cm^{-1} . These bands were attributed to the octahedral OH stretching vibrations (Madejova and Komadel 2001). In the fingerprint region, kaolinite revealed sharp bands at 1,105, 1,033, and 1,008 cm^{-1} attributed to the Si–O stretching and at 937 and 914 cm^{-1} corresponding to the OH deformation of hydroxyl groups. Most of the other bands such as the Si–O vibrations observed at 791, 698, 540, 470, and 430 cm^{-1} also confirmed the presence of kaolinite mineral. On the other hand, apparently, there were no significant changes in the FTIR spectrums of acid- and lime-treated samples. Nevertheless, due to the chemical attack, it seemed to be a slight decrease in the intensity of absorption band at 1,105 cm^{-1} . Furthermore, in lime-treated samples, a new absorption band at 1,385 cm^{-1} attributed to the Ca–OH bond of lime was evident (Nacamoto 1970).

In order to assess the degree of improvement in the white kaolin soil, UCS test was performed on phosphoric acid- and lime-treated samples (Ingles and Metcalf 1972). Analysis of the data presented in Fig. 6 revealed several interesting points. First of all, the lime mix designs obtained higher strength developments for all time intervals. Secondly, after 8 months of curing, with respect to 5% lime and phosphoric acid treatment, an increase of almost ten- and fivefold in the strength of stabilized soil in comparison with the natural soil was observed. The third point worth noting was the fact that for the 2% lime-treated samples, there was only a small gain in the strength from 4 to 8 months of curing. Finally, considering the effects of curing time, it was also evident that with further curing, there was a significant improvement in the strength of 5% acid- and lime-stabilized samples. This could be explained by the slow nature of soil-chemical reactions, which were mainly responsible for the formation of new reaction products that cemented the clay particles together.

4 Conclusions

In this paper, the efficacy of phosphoric acid and lime treatment and moreover the mechanisms responsible for the improvement of tropical kaolin soils were investigated.

Based on the data collected from leaching analysis, the kaolinite mineral with pH-dependent structural properties showed slightly different behavior both in basic and in acidic mediums. In lime treatment, negative charges were generated on the edges of clay particles. These negative sites, which were previously involved in hydrogen bonding to other mineral sheets, consequently attracted calcium ions in the pore water solution. On the other hand, the protonation of soil due to inclusion of phosphoric acid and its interaction with surface hydroxyl groups resulted in the formation of positive charges on the surface of clay particles. In addition, the alumina sites present in the 1:1 layer-type kaolinite mineral

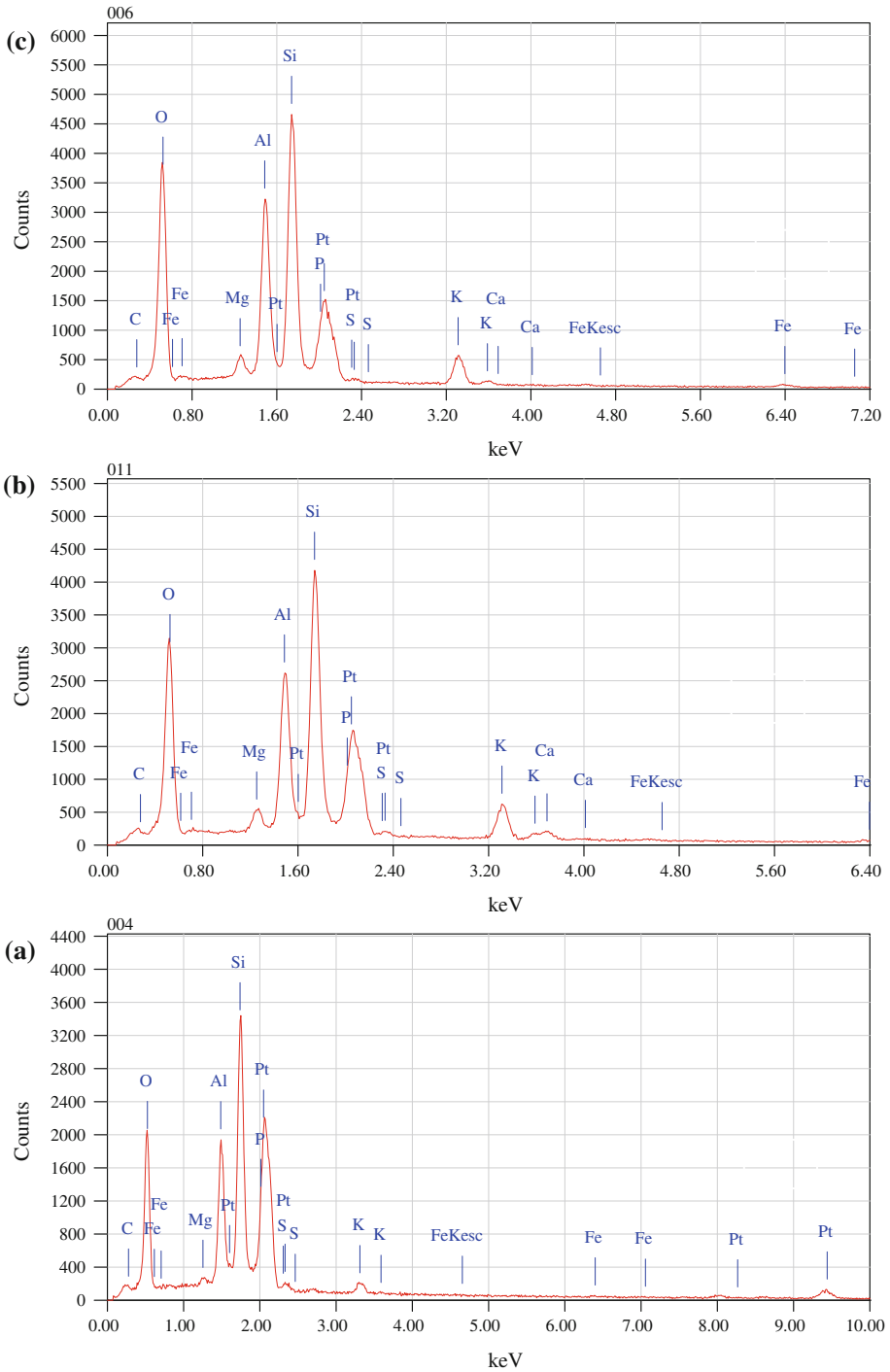


Fig. 3 EDAX spectra of **a** untreated **b** lime-treated and **c** phosphoric acid-treated kaolin

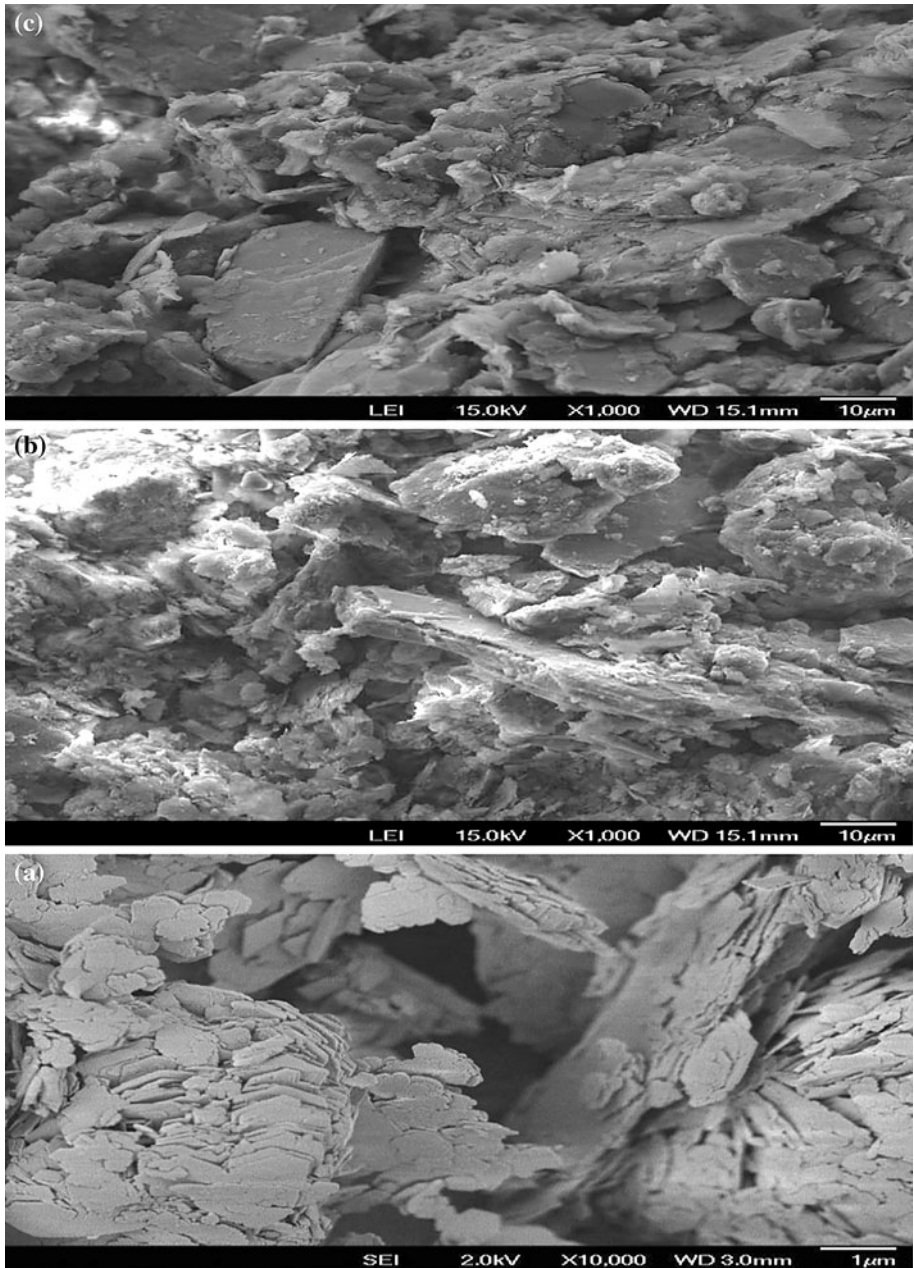


Fig. 4 FESEM images of **a** untreated, **b** lime-treated, and **c** phosphoric acid-treated kaolin after 8-month curing period

also contributed to the development of positive charges. As a result, these positive sites attracted phosphate ions present in the soil environment. The leaching test also revealed further important points regarding the longer-term development of reaction products. As

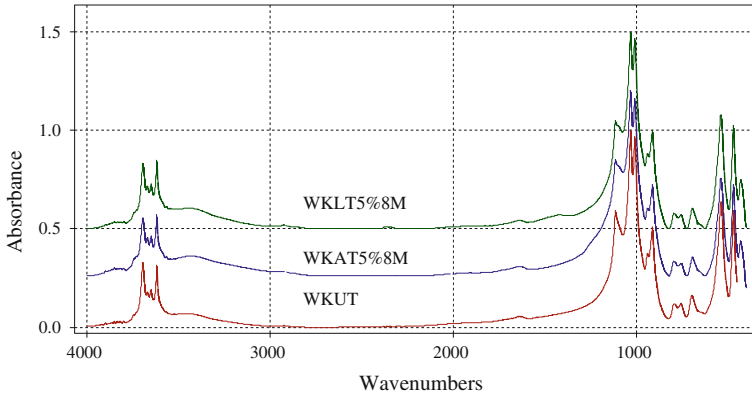


Fig. 5 FTIR spectrum of natural kaolin and 8-month-cured phosphoric acid- and lime-treated soil

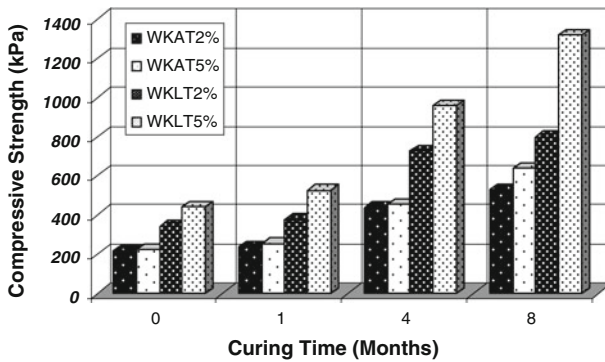


Fig. 6 Unconfined compressive strength (UCS) of lime- and phosphoric acid-treated kaolin soil with different stabilizer content and curing time

was evident from the results, the chemical stabilizers preferentially attacked the alumina surface of the clay particles. Therefore, it was rational to suggest that with respect to lime and phosphoric acid treatment, aluminates hydrate compounds were more likely to be formed. Also, it was found that after 8-month curing period, the phosphate and calcium ions introduced by the stabilizers were incorporated into the reaction products, making them less soluble in the pore water.

According to the FTIR results, the soil-stabilizer interactions at the particle level were mainly surface-associated and that there were no fundamental changes in the molecular structure of clay minerals.

From geotechnical point of view, the results obtained for unconfined compressive strength test clearly indicated a considerable improvement in the engineering properties of treated samples. In general, in comparison with acid stabilization, the lime-treated soil gained more strength for all curing times. Also, in soil samples treated at lime contents obtained by the initial consumption of lime (ICL) test, there was only a small gain in the strength at longer curing periods. The latter was caused by the lack of free calcium ions present in the soil environment to promote pozzolanic reactions.

In conclusion, based on the data obtained from various spectroscopic and microscopic techniques, it could be postulated that the primary ion-exchange reactions followed by a surface alteration of the clay structure were the main mechanisms responsible for the improvement in lime- and phosphoric acid-stabilized kaolin soil. In addition, the Ca/Si and P/Si ratios obtained from EDAX analysis suggested that there were significant changes in the surface composition of soil particles at different time intervals. This also emphasized the fact that the soil-stabilizer reactions were mainly surface-associated.

Acknowledgment This research was supported by the Ministry of Higher Education (MOHE), Malaysia under the Fundamental Research Scheme Grant Vot. 78011.

References

- Balasubramaniam AS, Bergado DT, Buensucos BR Jr, Yang WC (1989) Strength and deformation characteristics of lime treated soft clay. *J Geotechn Eng* 20:49–65
- Bell FG (1996) Lime stabilization of clay minerals and soils. *Eng Geol* 42(4):223–237
- Boardman DI, Glendinning S, Rogers CDF (2001) Development of solidification and stabilisation in lime-clay mixes. *Geotechnique* 40:533–543
- Brady NC, Weil RR (1996) The nature and properties of soils, 11th edn. Prentice Hall, New Jersey
- Brown G (1961) The X-ray identification and crystal structures of clay mineral. Mineralogical Society (Clay Minerals Group), London
- BSI (1990a) British standard methods of test for soils for civil engineering purposes: part 4, Compaction-related tests. BS1377, British Standards Institution, London
- BSI (1990) Stabilized materials for civil engineering purposes: part 2, Methods of test for cement-stabilized and lime-stabilized materials. BS1924, British Standards Institution, London
- Carroll D, Starkey HC (1971) Reactivity of clay minerals with acids and alkalis. *Clays Clay Miner* 19:321–333
- EC (1990) Compendium of waste leaching tests. Report EPS 3/HA/7. Environment Canada, Waste Water Technology Centre
- Eisazadeh A (2010) Physicochemical behaviour of lime and phosphoric acid stabilized clayey soils. Universiti Teknologi Malaysia (UTM), Ph.D. Thesis
- Herzog A, Mitchell JK (1963) Reactions accompanying the stabilization of clay with cement. *US Highw Res Board Bull* 36:146–171
- Ingles OG, Metcalf JB (1972) Soil stabilization—principles and practice. Butterworth, Melbourne
- JCPDS (1995) Index to the powder diffraction file. International center for diffraction data, Swarthmore
- Ioannou A, Dimirkou A (1997) Phosphate adsorption on Hematite, Kaolinite, and Kaolinite-Hematite (k-h) systems as described by a constant capacitance model. *J Colloid Interf Sci* 192:119–128
- Kota PBVS, Hazlett D, Perrin L (1996) Sulfate-bearing soils: problems with calcium-based stabilizers. Transportation research record 1546, TRB, National Research Council, Washington DC, pp 62–69
- Locat J, Tremblay H, Leroueil S (1996) Mechanical and hydraulic behaviour of a soft inorganic clay treated with lime. *Can Geotech J* 33:654–669
- Lyons JW, McEwan GJ (1962) Phosphoric acid in soil stabilization, part I. Effect on engineering properties of soils. Highway research board bulletin (soil stabilization with phosphorous compounds and additives) Washington DC, vol 318, pp 4–14
- Madejova J, Komadel P (2001) Baseline studies of the clay minerals society source clays: Infrared methods. *Clays Clay Miner* 49(5):410–432
- Manju CS, Narayanan Nair V, Lalithambika M (2001) Mineralogy, geochemistry and utilization study of the Madayi kaolin deposit, North Kerala, India. *Clays Clay Miner* 49(4):355–369
- Medina J, Guida HN (1995) Stabilization of lateritic soils with phosphoric acid. *J Geotech Geol Eng* 13:199–216
- Mitchell JK, Dermatas D (1992) Clay soil heave caused by lime-sulfate reactions. Innovations in uses for lime, ASTM STP 1135, American Society for Testing and Materials, Philadelphia, PA, pp 41–64
- Mitchell JK, Soga K (2005) Fundamentals of soil behavior, 3rd edn. Wiley, New York
- Nacamoto K (1970) Infrared spectra of inorganic and coordinated compounds. Wiley, New York
- Narasimha Rao S, Rajasekaran G (1996) Reaction products formed in lime-stabilized marine clays. *J Geotech Eng ASCE* 122:329–336

- Rajasekaran G, Narasimha Rao S (1997) The microstructure of lime-stabilized marine clay. *Ocean Eng* 24(9):867–878
- Rogers CDF, Glendinning S, Dixon N (1996) Lime stabilization. Proceedings of the seminar held at Loughborough University, Thomas Telford Publisher, London
- Rollings RS, Burkes JP, Rollings MP (1999) Sulfate attack on cement-stabilized sand. *J Geotechn Geoenviron Eng ASCE* 125(5):364–372
- Willoughby DR, Gross KA, Ingles OG, Silva SR, Veronica MS (1968) The identification of reaction products in alkali stabilized clay by electron microscopy, X-ray and electron diffraction. In: Proceedings of 4th conference of Australian board 4, part 2, pp 1386–1408