University Technology Malaysia

From the SelectedWorks of Hadi Nur

2010

Physicochemical characteristics of phosphoric acid stabilized bentonite

Amin Eisazadeh, University Technology Malaysia Khairul Anuar Kassim, University Technology Malaysia Hadi Hadi



Available at: https://works.bepress.com/hadi_nur/51/



Physicochemical Characteristics of Phosphoric Acid Stabilized Bentonite

Amin Eisazadeh

PhD in Geotechnical Engineering, Geotechnic & Transportation Department, Faculty of Civil Engineering, Universiti Teknologi Malaysia, Malaysia e-mail: A.Eisazadeh@yahoo.com

Khairul Anuar Kassim

Professor in Geotechnical Engineering, Geotechnic & Transportation Department, Faculty of Civil Engineering, Universiti Teknologi Malaysia, Malaysia e-mail: kanuar@utm.my

Hadi Nur

Associate Professor, Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, Malaysia e-mail: hadi@kimia.fs.utm.my

ABSTRACT

The expansive nature of soils containing high amounts of montmorillonite mineral can be altered through chemical stabilization, resulting in a material suitable for construction purposes. In this paper, the physicochemical behaviour of phosphoric acid treated samples was studied using X-ray Diffractometry (XRD), Energy Dispersive X-ray Spectrometry (EDAX), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), and Solid-State Nuclear Magnetic Resonance spectroscopy (SS-NMR). It was found that in acid stabilized montmorillonitic soil, clay alumina was more susceptible to dissolution and mostly responsible for the formation of aluminate phosphate hydrate compounds that bonded the soil particles together. Furthermore, since the action of stabilizer was mainly "surface-associated", the efficiency of phosphoric acid treatment in terms of strength improvement was rather limited.

KEYWORDS: Bentonite, Phosphoric acid, Stabilization, Characterization

INTRODUCTION

During past decade, depending on the nature and function of soil, many different chemical products have been proposed to stabilize the soil. However the use of acidic additives has been limited. This is due to the lack of standard laboratory work which makes it very difficult to evaluate their long-term performance. Nevertheless, phosphoric acid stabilization has been used occasionally on some roads in North America (The Missouri State Highway Department) and has shown good results (Ingles and Metcalf, 1972).

In general, acids are effective in removing alumina and other metallic oxides from clay minerals (Herzog and Mitchell, 1963). According to Lyons and McEwan (1962), when soluble phosphoric acid is added to a soil, it tends to undergo sequential reactions with the initially dissolved aluminum, precipitating phosphorus containing compounds. Furthermore, as the time passes, this water soluble salt reacts further to produce an insoluble cementitious gel. Thus the overall reaction at room temperature can be given as:

$$Al(OH)_{3} \text{ (from the clay lattice)} + 3H_{3}PO_{4} \rightarrow Al(H_{2}PO_{4})_{3} + 3H_{2}O$$

$$(1)$$

$$2Al(OH)_{3} \text{ (from Al}(H_{2}PO_{4})_{3}) + clay lattice \rightarrow 3AlPO_{4} \text{ (cement gel)} + 6H_{2}O$$

As a result of current understanding, various microscopic and spectroscopic test procedures were used in this paper to obtain the following objectives:

(a) To assess the changes induced on the mineralogy, morphology, and the elemental composition of treated samples by determining microstructural characteristics of soil-stabilizer matrix at the particle level.

(b) To study the molecular structure in terms of functional groups and local bonding in an attempt to evaluate the magnitude of stabilizer penetration into the crystalline clay structure and its interlayers.

MATERIALS AND METHODS

Materials

Less complex and more pure bentonite comprised mainly of sodium-montmorillonite mineral was used in this investigation (Eisazadeh, 2010). Sodium-montmorillonite has a high swelling capacity and forms gel-like masses when added to water (Grim and Guven, 1978). The bulk soil which is an odorless, greenish powder was purchased in 50 kg bags from Wyoming located in the Western province of United States. The chemical and physical properties of the natural soil are presented in Table 1. It should be noted that the phosphoric acid used in this research was a Merck analyzed, 85% H₃PO₄, of specific gravity 1.71.

Preparation of specimens

Based on the previous studies conducted on phosphoric acid stabilized soils (Medina and Guida, 1995), three percentages of acid (i.e., 1%, 3% and 7%) by weight of the dry soil were chosen for this investigation. Mix designs required for different laboratory analyses were then compacted as specified in clause 4.1.5 of BS 1924: Part 2: 1990. After completion of compaction they were wrapped in a cylindrical PVC tubes (50 mm diameter \times 100 mm length) and sealed to the atmosphere with rubber tight lids. The samples were then stored in a thermostatically controlled room (27±2°C) until being tested at 1 month, 4 months, and 8 months time interval. In order to effectively present the obtained results, a specimen designation scheme was used. Letters in the specimen designation indicated soil name, type of treatment, and curing period, respectively (i.e., GB: green bentonite, AT: acid treated, M: months).

Physical Properties	Values	Chemical Composition (oxides)	Values (%)
CEC (meq/100 g)	78.79	SiO ₂	60.79
pH (L/S = 2.5)	9.03	Al_2O_3	21.20
Specific Gravity	2.64	Fe ₂ O ₃	6.46
Liquid Limit, LL (%)	301.60	CaO	0.96
Plastic Limit, PL (%)	41.80	MgO	3.26
Plasticity Index, PI (%)	259.80	Na ₂ O	6.14
BS Classification	CE	CO_2	1.19
ICL (%)	7.00		
Maximum dry density (Mg/m ³)	1.27		
Optimum moisture content (%)	37.70		
Unconfined compressive strength (kPa)	281.30		

Table 1: Engineering properties and chemical composition of the natural Bentonite

Testing program

In this research, a Bruker D8 advance diffractometer was used to perform scans in an angle scan (2 θ) ranging between 6° to 90° with a 0.02° step size and dwelling time of one second at each step. At the end of the test, the mineralogy analysis was carried out based on the characteristic Bragg data available in the standard powder diffraction file (JCPDS, 1995).

A JSM-6701F JEOL field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray spectrometer (EDAX) was employed to study the topographic features and the chemical changes associated with the surface of soil particles, respectively. The sample preparation for both techniques involved drying the samples and placing them onto an aluminum stub covered with double-sided carbon tape, and coating the specimen with platinum using a vacuum sputter coater in order to prevent surface charging and loss of resolution.

Fourier transform infrared spectroscopy has a long and successful history as an analytical technique and has been applied in the study of clay minerals (Farmer and Russell, 1964; Farmer, 1974). FTIR was performed using a Perkin Elmer Spectrum 2000 instrument. The technique involved drying the samples and mixing the solid residue with potassium bromide (KBr) to form a homogeneous powder, which was then compressed into a solid pellet. The pellet was placed in a sample holder where it was scanned by infrared radiation (IR) to yield a pattern of the beam transmitted through the sample from 400 to 4000 cm⁻¹.

High-resolution solid state nuclear magnetic resonance (SS-NMR) spectroscopy has become a powerful tool in studying the structure of variety of clay minerals such as montmorillonite (Barron *et al.*, 1985; Kinsey *et al.*, 1985; Engelhardt and Michel, 1987). In this paper, the ²⁷Al MAS NMR spectra of natural and phosphoric acid treated samples were recorded after 8 months of curing. The spectra were obtained by a Bruker AVANCE 400 MHz solid-state NMR instrument using a MAS probe with 7 mm Zirconium rotor.

RESULTS AND DISCUSSION

XRD graphs of natural and phosphoric acid treated bentonite after 8 months of curing are shown in Figure 1. As can be seen, the major clay mineral present in the soil environment was montmorillonite $(2\theta \approx 8^{\circ}, 21^{\circ}, 28^{\circ}, 35^{\circ}, 62^{\circ})$, and illite $(2\theta \approx 9^{\circ}, 22^{\circ}, 42^{\circ})$ (Brown, 1961). Other reflections observed at approximately 22°, 27°, and 29.4° 20 corresponded to crystoballite, quartz, and calcite, respectively. The qualitative analysis of the XRD results indicated that after application of acid, the characteristic peaks of montmorillonite $(2\theta \approx 8^{\circ})$ and illite $(2\theta \approx 9^{\circ})$ appeared to have vanished. In addition, there were slight decreases in the intensity of other peaks corresponding to these minerals. Furthermore, after 8 months of curing, several new peaks at various 20 angles, i.e., 30.7° , 32° , and 33.7° were observed. These peaks were assigned to aluminate phosphate hydrate compounds.



Figure 1: XRD patterns for untreated and 8 months cured phosphoric acid treated Bentonite

EDAX spectrums of the untreated (GBUT) and 8 months cured bentonite containing 7% phosphoric acid (GBAT7%8M) are shown in Figure 2. As can be seen, aluminum (Al), silicon (Si), magnesium (Mg), sodium (Na), iron (Fe), and calcium (Ca) peaks were clearly evident in the natural soil. The presence of these elements along with their intensity confirmed the dominancy of montmorillonite mineral in the soil medium (Carroll and Starkey, 1971). In addition, the acid treated samples also contained phosphorous (P). The presence of phosphorous was consistent with the application of phosphoric acid to the soil medium.

In Figure 3, the morphology of phosphoric acid treated bentonite after 1 and 8 months of curing are shown. As can be seen, due to the treatment the soil fabric has transformed from a flake based form into a more flocculated structure. In addition, in 8 months cured samples, the weathering action of acid on the edges of clay particles was clearly evident.





Figure 2: EDAX spectra of untreated (bottom) and phosphoric acid treated (top) Bentonite



Figure 3: FESEM images of phosphoric acid treated Bentonite at different time intervals*cont'd in next page.*



Figure 3: FESEM images of phosphoric acid treated Bentonite at different time intervals

FTIR spectra of natural and phosphoric acid stabilized bentonite soil in the middleinfrared region (400-4000 cm⁻¹) are presented in Figure 4. As shown, the KBr curve of untreated sample was characteristic of montmorillonite mineral with a single sharp band at 3632 cm⁻¹, followed by a broad band at 3446 cm⁻¹ for OH stretching of structural hydroxyl groups and water, respectively (Madejova and Komadel, 2001). In the lower frequency region, montmorillonite also had a strong band at 1050 cm⁻¹ for Si-O stretching (in-plane) vibration of layered silicates. The absorption peak in the 1640 cm⁻¹ region was attributed to the OH deformation mode of water. IR peaks at 913 cm⁻¹ and 885 cm⁻¹ were attributed to AlAlOH and AlFeOH, respectively. The 466 cm⁻¹ band was a Si-O-Si deformation, and the band at 524 cm⁻¹ corresponded to the deformation mode of Al-O-Si group. The 620 cm⁻¹ band was a coupled Al-O and Si-O (out-of-plane) bond. There were also some quartz present as indicated by the bands at 778 cm⁻¹ and 791 cm⁻¹ (Marel and Beutelspacher, 1976). Assessment of the FTIR spectrums in acid treated samples indicated few noticeable changes. First of all, there were a slight decrease in the intensity of AlAlOH bond and a distortion at 620 cm⁻¹ absorption band with curing time. These changes were probably caused by the action of stabilizer on the clay structure. In addition, new peak at 2920 cm⁻¹ with respect to 8 months cured samples was evident. The latter was assigned to the P-OH bond of phosphoric acid present in the soil-stabilizer matrix (Nacamoto, 1970).



Figure 4: FTIR spectrums of untreated and phosphoric acid treated samples

In this research, ²⁷Al MAS NMR spectroscopy was performed in order to determine the local structure around the Al atoms. As can be seen in Figure 5, the spectrum of untreated Green Bentonite showed a relatively sharp symmetric band at approximately 57 ppm corresponding to the tetrahedrally coordinated Al, and a broad peak at 2 ppm arising from octahedral Al (Okada *et al.*, 2006). After 8 months of curing, the ²⁷Al NMR spectra revealed the same tetrahedral peak to the original peak with a slight shift to the right. This suggested a similar local structure to the original structure of the natural soil.



Figure 5: ²⁷Al MAS NMR spectra of the natural and 8 months cured bentonite

Figure 6 shows the unconfined compressive strength of phosphoric acid treated Bentonite soil under different stabilizer content and curing time conditions. It was clear that the stabilization technique was effective in improving the strength properties of the soil. For instance, following the acid treatment, where an amount of 7% by weight of the soil was incorporated into the mix design, compressive strength of 758 kPa after 8 months time period was obtained which was 2.8-fold higher than the untreated sample.



Figure 6: Time-dependent strength development for phosphoric acid treated Bentonite

CONCLUSIONS

Based on the results, it could be concluded that the phosphoric acid particles preferentially attacked the alumina surface of montmorillonite mineral structure which resulted in the formation of aluminate phosphate hydrate compounds with curing time. Furthermore, the soil-acid reactions were mainly "surface-associated" and restricted to the edges of clay particles which consequently limited the degree of soil improvement. The latter was due to the fact that in montmorillonite mineral the source of alumina is sandwiched between the two silica layers (Figure 7).



Figure 7: Interaction between acid particles and the montmorillonite mineral strucutre

REFERENCES

1. Barron, P.F., Slade, P., and Frost, R.L. (1985) "Solid-state silicon-29 spin-lattice relaxation in several 2:1 phyllosilicate minerals." Journal of Physical Chemistry, 89, 3305–3310.

- 2. Brown, G. (1961) "The x-ray identification and crystal structures of clay mineral." (Mineralogical Society, London)
- 3. BSI1924, (1990) "Stabilized materials for civil engineering purposes." (British Standards Institution: London)
- 4. Carroll, D., and Starkey, H.C. (1971) "Reactivity of clay minerals with acids and alkalies." Clays and Clay Minerals, 19, 321–333.
- 5. Eisazadeh, A. (2010) "Physicochemical behaviour of lime and phosphoric acid stabilized clayey soils." PhD Thesis, Universiti Teknologi Malaysia (UTM), Malaysia.
- 6. Engelhardt, G., and Michel, D. (1987) "High resolution solid state NMR of silicates and zeolites." (Wiley: Chichester, United Kingdom)
- 7. Farmer, V.C., and Russell, J.D. (1964) "The infrared spectra of layer silicates." Spectrochimica Acta, 20, 1149–1173.
- 8. Farmer, V.C. (1974) "The Infrared Spectra of Minerals. Monograph 4." (Mineralogical Society: London)
- 9. Grim, R.E., and Guven, N. (1978) "Bentonites geology, mineralogy, properties and uses." (Elsevier Scientific: Amsterdam)
- 10. Herzog, A., and Mitchell, J.K. (1963) "Reactions accompanying the stabilization of clay with cement." United State Highway Research Board Bulletin, 36, 146–171.
- 11. Ingles, O.G., and Metcalf, J.B. (1972) "Soil stabilization principles and practice." (Butterworth: Melbourne, Australia)
- 12. JCPDS, (1995) "Index to the powder diffraction file." (International Center for Diffraction Data: Swarthmore, Pa)
- Kinsey, R.A., Kirkpatrick, R.J., Hower, J., Smith, K.A., and Oldfield, E. (1985) "High resolution aluminum-27 and silicon-29 nuclear magnetic resonance spectroscopic study of layer silicates, including clay minerals." American Mineralogist, 70, 537–548.
- Lyons, J.W., and McEwan, G.J. (1962) "Phosphoric acid in soil stabilization, part I. Effect on engineering properties of soils." Highway Research Board Bulletin, 318, 4– 14.
- 15. Madejova, J., and Komadel, P. (2001) "Baseline studies of the clay minerals society source clays: Infrared methods." Clays and Clay Minerals, 49(5), 410–432.
- 16. Marel, H.W.V.D., and Beutelspacher, H. (1976) "Atlas of infrared spectroscopy of clay minerals and their admixtures." (Elsevier Scientific Publishing: Amsterdam)
- 17. Medina, J., and Guida, H.N. (1995) "Stabilization of Lateritic soils with phosphoric acid." Journal of Geotechnical and Geological Engineering, 13, 199–216.
- Nacamoto, K. (1970) "Infrared spectra of inorganic and coordinated compounds." (Wiley: New York)
- Okada, K., Arimitsu, N., Kameshima, Y., Nakajima, A., and MacKenzie, K.J.D. (2006) "Solid acidity of 2:1 type clay minerals activated by selective leaching." Applied Clay Science, 31, 185–193.



335

© 2010 ejge

