

University Technology Malaysia

From the Selected Works of Hadi Nur

2010

Molecular Characteristics of Phosphoric Acid Treated Soils

Amin Eisazadeh, *University Technology Malaysia*

Khairul Anuar Kassim, *University Technology Malaysia*

Hadi Nur, *University Technology Malaysia*



Available at: https://works.bepress.com/hadi_nur/53/

Molecular Characteristics of Phosphoric Acid Treated Soils

Amin Eisazadeh^a, Khairul Anuar Kassim^a, and Hadi Nur^b

Abstract—The expansive nature of soils containing high amounts of clay minerals can be altered through chemical stabilization, resulting in a material suitable for construction purposes. The primary objective of this investigation was to study the changes induced in the molecular structure of phosphoric acid stabilized bentonite and lateritic soil using Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FTIR) spectroscopy. Based on the obtained data, it was found that a surface alteration mechanism was the main reason responsible for the improvement of treated soils. Furthermore, the results indicated that the Al present in the octahedral layer of clay minerals were more amenable to chemical attacks and also partly responsible for the formation of new products.

Keywords—Bentonite, Laterite clay, Molecular characterization, Phosphoric acid, Stabilization

I. INTRODUCTION

WITH the reduction of available land resources, more and more construction of civil engineering structures is carried out over soft clay deposits which are found in many parts of the world. In such problematic soils, chemical stabilization techniques have proven to be effective [1]. 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. Also as reported in previous studies, phosphoric acid stabilization is a potentially attractive alternative for treating lateritic soils [2]-[4]. This is due to the reaction of phosphoric acid with free iron and aluminum oxides present in the soil environment [5].

Infrared (IR) spectroscopy has a long and successful history as a complementary method to X-ray diffraction (XRD) and other methods used to investigate clays [6], [7]. An IR spectrum can serve as a fingerprint for mineral identification, but it can also give unique information about the mineral structure, including the family of minerals to which the specimen belongs and the degree of regularity within the structure, the nature of isomorphous substituents, the distinction

of molecular water from constitutional hydroxyl, and the presence of both crystalline and non-crystalline impurities [8].

High-resolution Solid-State Nuclear Magnetic Resonance (SS-NMR) spectroscopy has become a powerful tool in studying the structure of natural aluminosilicates [9], [10]. In particular, ²⁹Si and ²⁷Al Magic-Angle-Spinning (MAS) NMR have provided important information on the Si and Al distribution in tetrahedral and octahedral sites, the sequences of charged sheets, and the structural distortions for variety of clay minerals [11]-[13]. Nonetheless, much less attention has been devoted to NMR studies of chemically stabilized soils.

In this paper, in order to understand the main mechanisms that contributed to the improvement of phosphoric acid stabilized bentonite and lateritic soils, the time-dependent changes occurring in the molecular structure of treated soils were investigated.

II. MATERIALS AND EXPERIMENTAL PROGRAM

A. Materials

Pure bentonite soil comprised mainly of sodium montmorillonite mineral and a residual lateritic soil with high amounts of iron oxides were used in this investigation. The chemical and physical properties of the natural soils are presented in Table 1. It should be noted that the phosphoric acid was a Merck analysed, 85% H₃PO₄, of specific gravity 1.71.

B. Preparation of specimens

In order to determine the compaction characteristics of the untreated soil a standard compaction test in accordance with clause 3.3.4.1 of BS 1377: Part 4: 1990 was performed [14]. This resulted in a compactive effort of 596 kJ/m³ being applied. Samples required for different laboratory analyses were then prepared and compacted to a constant compactive effort in a cylindrical thin wall PVC tubes (50 mm diameter × 100 mm length) as specified in clause 4.1.5 of BS 1924: Part 2: 1990 [15]. After completion of compaction they were wrapped with thin plastic film 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 curing period. Also in order to effectively present the obtained results, a specimen designation scheme was used. Letters in the specimen designation indicated soil name and type of treatment, respectively (i.e., GB: Green Bentonite, LC: Laterite Clay, AT: acid treated, M: months).

^a Geotechnic & Transportation Department, Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia (Corresponding author, Tel.: +60177080315; fax: +6075566157; e-mail: A.Eisazadeh@yahoo.com)

^b Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

C. Testing program

In this research, FTIR was performed for all stabilized soils 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 waves per centimeter (cm^{-1}). In addition, the ^{27}Al MAS NMR spectra of 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 7mm Zirconium rotor.

III. RESULTS AND DISCUSSION

FTIR spectra of natural and treated samples are presented in Fig. 1. As can be seen, the KBr curve of untreated Green Bentonite 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 [16]. In Laterite Clay, the presence of kaolinite mineral with strong bands at different wavelength (cm^{-1}) was apparent. There were also some quartz present as indicated by the bands at 778 cm^{-1} and 791 cm^{-1} [17]. Assessment of the FTIR spectrums in phosphoric acid treated samples indicated no noticeable changes with curing time. However, in 8 months cured bentonite samples, a new peak at 2920 cm^{-1} due to phosphoric acid treatment was evident [18].

^{27}Al MAS NMR spectra of 8 months cured Green Bentonite and Laterite Clay samples are presented in Fig. 2. The test was carried out in order to determine the local structure around the Al atoms. In contrast to the Laterite Clay samples, the ^{27}Al NMR spectrum of the Bentonite soil revealed a relatively sharp symmetric band at approximately 57ppm corresponding to the tetrahedrally coordinated Al, and a small peak at 2ppm arising from octahedral Al. On the other hand, the intensity of octahedral peak in laterite samples supported the presence of kaolinite mineral with 1:1 silica: alumina structure in the soil environment.

TABLE I
PHYSICOCHEMICAL PROPERTIES OF THE NATURAL SOIL

PHYSICAL PROPERTIES	VALUES	
	Green Bentonite	Laterite Clay
CEC (meq/100 g)	78.79	14.88
pH (L/S = 2.5)	9.03	4.86
Liquid Limit, LL (%)	301.60	75.8
Plastic Limit, PL (%)	41.80	39.60
Plasticity Index, PI (%)	259.80	36.20
IS Classification	CE	MH
ICL (%)	7	5
Maximum dry density (Mg/m^3)	1.27	1.33
Optimum moisture content (%)	37.70	34.00
UCS (Untreated (kPa))	281	288
UCS (8 months cured (kPa))	758	843
CHEMICAL COMPOSITION (Oxides)	VALUES (%)	
	Green Bentonite	Laterite Clay
SiO ₂	60.79	21.55
Al ₂ O ₃	21.20	24.31
Fe ₂ O ₃	6.46	29.40
MgO	3.26	*
Na ₂ O	6.14	0.07
CO ₂	1.19	3.65
P ₂ O ₅	*	16.71
K ₂ O	*	0.11
SO ₃	*	3.98
* Not detected		

IV. CONCLUSIONS

The FTIR spectrums of treated samples suggested that the stabilization process did not cause any major alterations in the functional groups of clay minerals. On the other hand, according to the ^{27}Al NMR results, it was found that the Al present in the octahedral layer of clay minerals were more amenable to chemical attacks and also partly responsible for the formation of new products. This was also consistent with higher strength gains achieved for acid stabilized lateritic soil over 8 months curing period (Table 1).

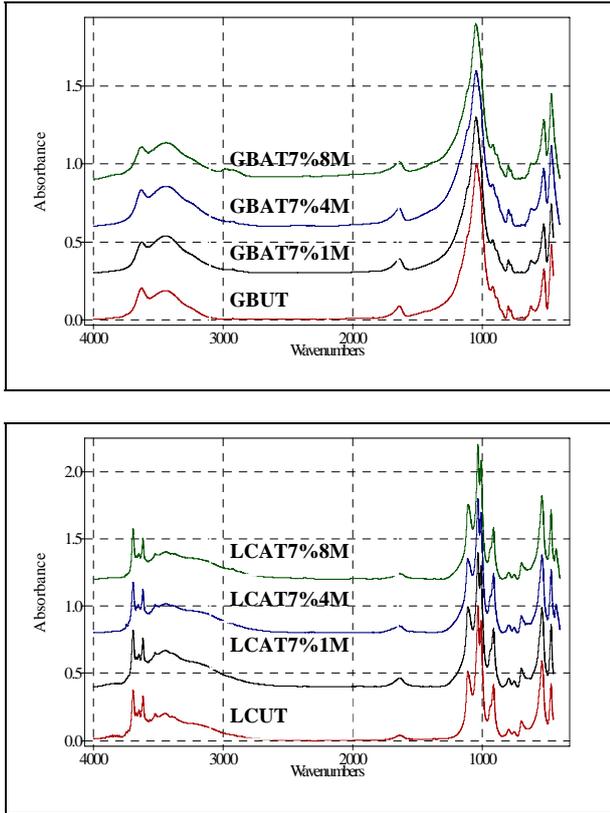


Fig. 1 FTIR of natural and 1, 4, and 8 months cured samples.

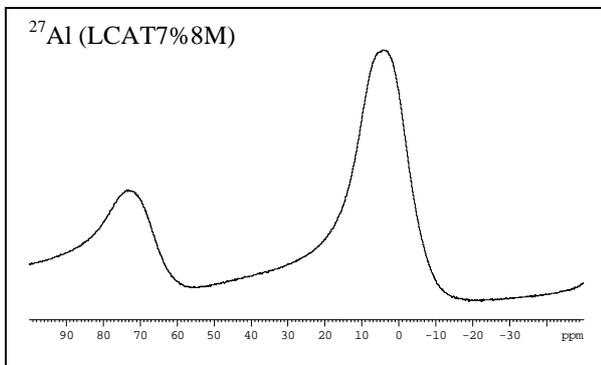
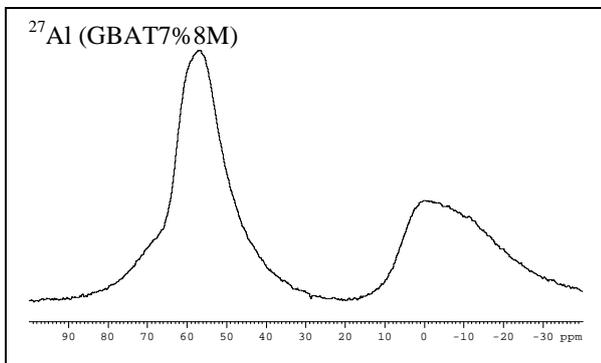


Fig. 2 ²⁷Al MAS NMR spectra of 8 months cured Green Bentonite (GB) and Laterite Clay (LC).

REFERENCES

- [1] O. G. Ingles and J. B. Metcalf, *Soil stabilization - principles and practice*, Melbourne: Butterworth, 1972.
- [2] J. W. Lyons and G. J. McEwan, "Phosphoric acid in soil stabilization, part I. Effect on engineering properties of soils," *Highway Research Board Bulletin 318*, Washington, D.C., 1962, pp. 4-14.
- [3] J. Sutton and E. McAlexander, "Soil improvement committee - Admixture report," *Geotechnical Special Publication No. 12*, New York: ASCE, 1987, pp. 123-124.
- [4] J. Medina and H. N. Guida, "Stabilization of Lateritic soils with phosphoric acid," *Journal of Geotechnical and Geological Engineering*, vol. 13, 1995, pp. 199-216.
- [5] H. F. Winterkorn, "Introductory remarks," *Highway Research Board Bulletin 318*, Washington, D.C., 1962, pp. 1-3.
- [6] M. L. McKelvy, T. R. Britt, B. L. Davis, J. K. Gillie, L. A. Lentz, A. Leugers, R. A. Nyquist, and C. L. Putzig, "Infrared Spectroscopy," *Analytical Chemistry*, vol. 68, 1996, pp. 93-160.
- [7] B. Stuart, *Modern Infrared Spectroscopy*, New York and UK: John Wiley & Sons, 1996.
- [8] V. C. Farmer, *The Infrared Spectra of Minerals*, London: Mineralogical Society, 1974.
- [9] R. A. Kinsey, R. J. Kirkpatrick, J. Hower, K. A. Smith, and E. Oldfield, "High resolution aluminum-27 and silicon-29 nuclear magnetic resonance spectroscopic study of layer silicates, including clay minerals," *American Mineralogist*, vol. 70, 1985, pp. 537-548.
- [10] G. Engelhardt and D. Michel, *High resolution solid state NMR of silicates and zeolites*, UK: John Wiley & Sons, 1987.
- [11] P. F. Barron, P. Slade, and R. L. Frost, "Solid-state silicon-29 spin-lattice relaxation in several 2:1 phyllosilicate minerals," *Journal of Physical Chemistry*, vol. 89, 1985, pp. 3305-3310.
- [12] C. P. Herrero, J. Sanz, and J. M. Serratos, "Tetrahedral cation ordering in layer silicates by ²⁹Si NMR spectroscopy," *Solid State Communications*, vol. 53, 1985, pp. 151-154.
- [13] C. A. J. Weiss, S. P. Altaner, and R. J. Kirkpatrick, "High-resolution ²⁹Si NMR spectroscopy of 2:1 layer silicates: Correlations among chemical shift, structural distortions, and chemical variations," *American Mineralogist*, vol. 72, 1987, pp. 935-942.
- [14] BSI, "British Standard methods of test for soils for civil engineering purposes: Part 4, Compaction-related tests," *BS1377*. London: British Standards Institution, 1990.
- [15] BSI, "Stabilized materials for civil engineering purposes: Part 2, Methods of test for cement-stabilized and lime-stabilized materials," *BS1924*. London: British Standards Institution, 1990.
- [16] J. Madejova and P. Komadel, "Baseline studies of the clay minerals society source clays: Infrared methods," *Clays and Clay Minerals*, vol. 49, no. 5, 2001, pp. 410-432.
- [17] H. W. V. D. Marel and H. Beutelspacher, *Atlas of infrared spectroscopy of clay minerals and their admixtures*, Amsterdam: Elsevier Scientific Publishing Company, 1976.
- [18] K. Nacamoto, *Infrared spectra of inorganic and coordinated compounds*, New York: John Wiley & Sons, 1970.