

Effect of Humic Acid on Microstructure of Lime-Treated Organic Clay

Nor ZurairahettyMohdYunus

Faculty of Civil Engineering, UniversitiTeknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia.

DariuszWanatowski

Department of Civil Engineering, Faculty of Science and Engineering, The University of Nottingham Ningbo, China

RodStace

Nottingham Centre for Geomechanics, Faculty of Engineering, The University of Nottingham, United Kingdom.

Norliana Abdullah

Faculty of Civil Engineering, UniversitiTeknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia.

RiniAsnida Abdullah

Faculty of Civil Engineering, UniversitiTeknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia.

Abstract

To date, there is no evidence of microstructural analysis conducted to help explain the effect of humic acid on the engineering behaviour of lime treated clay. This paper aims at investigating the changes in soil structure and chemical compositions of selected specimens of lime-treated organic clay with various humic acid contents. Scanning Electron Microscope (SEM) and X-ray diffractometer (XRD) analyses were carried out to reveal the microstructure of treated specimens. The SEM photographs of lime-treated organic clays show similar soil structure to that of untreated specimens where the cementing structure was hardly identified. However, the appearance of cracks in the untreated clay with 1.5% and 3.0% humic acid improved after the samples were treated with 5% lime. The evidence of cementing structures was only observed from XRD analysis. These observations showed that lime is less effective to stabilize clay with the presence of humic acid.

Keywords: Organic Clay; Humic Acid; Lime Stabilization; SEM; XRD.

1. Introduction

To date, there is little evidence in the literature of direct or indirect discussed on the use of microstructure analysis in investigating the behaviour of lime treated organic clay (Choquette et. al 1987; Rajasekaran and Rao, 1996; Onitsuka et al., 2001, Rajasekaran et al., 1996; James et al., 2007). In addition, none research has been conducted to investigate the effect of organic matter, specifically humic acid on the basis of microstructure study on the behaviour of lime treated clay. In particular, humic acid is a well-known constituent of organic matter with the potential to disrupt the soil stabilisation process. In fact, it has been reported that, more than 1% humic acid content in clay may render lime stabilisation process ineffective (Huat et al., 2005; Koslanant et al., 2006; Harris et al., 2009; Zhu et al., 2009; MohdYunus et al., 2012). This is because humic acid interferes with the pozzolanic reaction process between lime and clay by hindering or retarding it. To elaborate further, it causes a reduction in the pH of the mixtures pore solution. The effect of a highly alkaline environment (if permitted) is that it prolongs the dissolution of silica and alumina. The mechanism by which organic matter interferes with the strength development of lime-stabilised soil is not fully understood; therefore there is a need for a comprehensive study specifically in this area, as suggested by Huat et al. (2005). In addition, it has

also been suggested that the microstructure effect of various inorganic additives should be studied in more detail (Rajasekaran and Rao 1997).

The reaction between lime and clay occurs in two phases: modification and stabilisation (Uppal and Chad. 1967; Choquette et al., 1987; Bell, 1996; Rogers and Glendinning, 1997; Petry and Glazier 2002; James et al., 2008). The key reactions occurring in lime-treated clay are soil hydration, ion exchange, flocculation, and pozzolanic reaction (Boardman et al., 2001; Mallela et al., 2001; Onitsuka et al., 2001; Kumar et al., 2007, Sakr et al., 2009). In this paper, the effect of humic acid on the chemical process involved during lime-clay reaction will be examined using SEM and XRD microstructure analysis.

2. Materials

Artificial organic clay (untreated) used in this study was prepared by mixing a commercial kaolin with 0%, 0.5%, 1.5% and 3.0% commercial humic acid contents according to the dry mass of kaolin. The chemical elements present in each soil mixture are given in Table 1. Each type of soil was treated with 5% hydrated lime. In general, the effect of humic acid on the chemical elements present in organic clay can be detected from the increase in carbon and oxide ions.

Table 1. Chemical elements in the tested soils.

Element	Wt%			
	K	K 0.5HA	K 1.5HA	K 3.0HA
C	2.12	2.8	2.74	20.16
O	47.91	50.45	54.54	48.97
Na	0.2	0.36	0.41	0.81
Mg	0.64	0.65	0.64	0.56
Al	19.43	16.94	18.47	12.8
Si	26.71	24.74	21.52	14.07
P	0.09	0.18	0.28	0.16
S	0.02	0.05	0.12	0.42
Cl	0	0	0.01	0.19
K	2.65	3.42	0.79	0.59
Ca	0.02	0.02	0.04	0.33
Ti	0	0	0.02	0.18
V	0	0	0.01	0.01
Fe	0.21	0.39	0.4	0.74

3. Specimen Preparation

All the testing was carried out using FEI Quanta 600 Scanning Electron Microscope (SEM). The SEM facilitated the surface imagery of clay samples by scanning them with high-energy beam of electrons. The output image was based on the interaction between the electron signals and the sample atoms. Specimens analysed were directly

obtained from strength tests (UCS or triaxial) with no considerable specimen preparation required. Individual specimens were placed on a metal stud and coated with an ultrathin coating of electrically-conducting (carbon) material. The purpose of the coating is to increase the signal and surface resolution during scanning. Images were taken at series of magnification for the maximum possible clarity. Additionally individual chemical elements were analysed quantitatively using the built-in Energy Dispersive X-Ray (EDX) Spectrometers.

Furthermore, X-ray diffractometer (XRD) analysis was carried out to further verify the amount of chemical compositions with regards to the intensity of cementing materials present in the samples. For the XRD analysis, the specimens were crushed into fine powder, placed into sample holders and immediately x-rayed in the XRD machine. Each sample was analysed by observing their chemical compositions. Individual samples were then scanned through a range of diffraction pattern (two-theta-2 θ), considering that minerals are specified with each having a unique d-spacing. The changes in mineralogical compositions could be identified from the formation of cementitious products such as calcium aluminate hydrate (CAH), calcium silicate hydrate (CSH) and calcium aluminate-silicate hydrate (CASH).

4. Results and Discussions

Lime stabilisation normally alters soil properties such as the shear strength. Although the main interest in this paper is to study the changes in microstructure of lime-treated organic clay, some results related to the shear strength determined by the Unconfined Compressive Strength (UCS) testing are also shown here. Microstructure analysis was then performed on selected specimens to verify the results given by engineering testing.

The results of the UCS tests carried out on lime-treated organic clay with different humic acid contents (0%, 0.5%, 1.5%, 3%) and lime contents (5%, 8%, 10%, 15%) after 7 curing days are shown in Fig. 1. It can be seen that the undrained shear strength of all the specimens with 5% lime content increased significantly compared to the strength of untreated clay (i.e., 0% lime). However, the shear strength of specimens with higher than 5% lime contents reduced gradually with increasing lime content regardless of the humic acid content in the clay. Therefore, 5% was considered as the optimum lime content (OLC) for each type of organic clay. Figure 1 also shows that the shear strength of organic clay decreases with increasing humic acid content which proves that the presence of humic acid in organic clay diminishes the shear strength. Initial conclusion based on 7 curing days suggests the effectiveness of lime stabilisation in organic

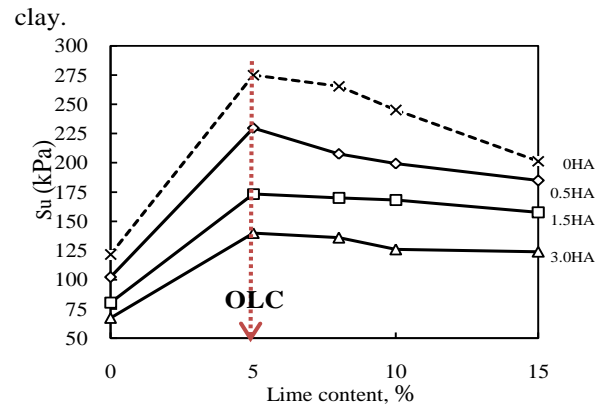


Figure 1. Effect of lime content on the shear strength of clay at 7 days of curing.

clay. Since the OLC for each specimen was similar therefore further investigation on the development of lime-clay reaction with time was only determined for 5% lime content. Figure 2 presents the undrained shear strength of lime-treated specimens after 7, 28 and 90 days. It appears that, except for inorganic clay (0% humic acid), the undrained shear strength of lime-treated organic clays with 0.5%, 1.5% and 3.0% humic acid contents decrease as time prolonged. For example, the strength at 7 curing days reduced from 230 kPa, 174 kPa and 140 kPa to 212 kPa, 130 kPa and 96 kPa at 90 days for specimens with 0.5%, 1.5% and 3.0% humic acid contents respectively. Despite exhibiting the loss in strength at longer periods, the strength at 90 curing days is still higher than that of the untreated specimens. However, for practical purpose, it is not a good idea to consider lime stabilisation as successful when the strength at long term is uncertain.

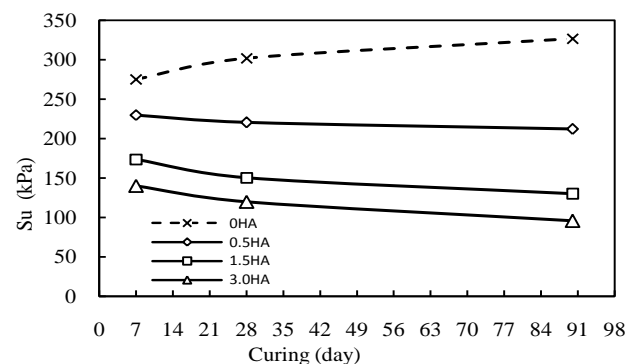


Figure 2. Effect of curing period on the undrained shear strength of lime-treated organic clay.

4.1. Microstructure of Lime-treated Specimens

A microscopic investigation of the soil microstructure of the lime-treated samples was carried out. Only images captured at 50000x magnifications were presented in this section. This

is because visual observation revealed an image scanned at 50000x magnification to be the most appropriate to provide a detailed description of the changes in the soil structure caused by the soil modification process. At the abovementioned magnification the clearest visual representation was displayed, aiding more detailed discussion. In addition, at 50000x magnification, the soil's particles individually correspond to a grain size of 2 μ m which also the representative size of a clay particle.

Figure3 to Figure6 show SEM images of the untreated inorganic clay (i.e., 0% humic acid content) and of untreated organic clays with 0.5%, 1.5% and 3.0% humic acid, respectively. As mentioned previously, images were taken 50000x magnification. Figure3 and Figure4 show a soil structure of sample without and with 0.5% humic acid content. It can be seen from these figures that both specimens have similar microstructures. Plate-like and hexagonal individual particles were observed in both clay specimens. A similar observation was reported by James et al. (2007) who found that a low humic acid content does not affect significantly the microstructure of clay. The fabrics of both specimens also reveals no apparent aggregations, which confirms the absence of chemical reactions in the untreated specimens.

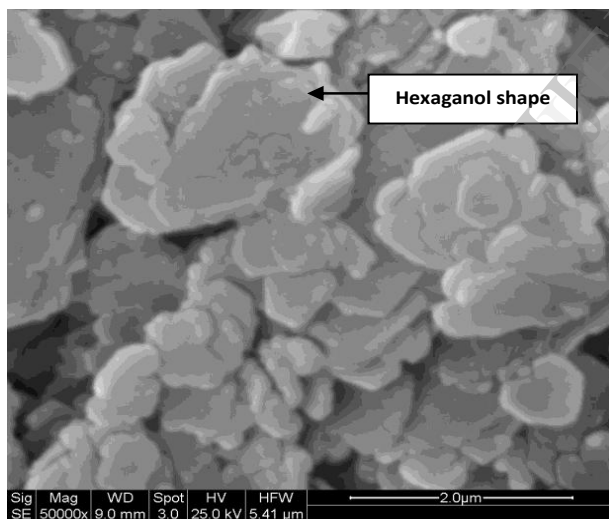


Figure3.SEM micrograph of untreated clay without humic acid content.

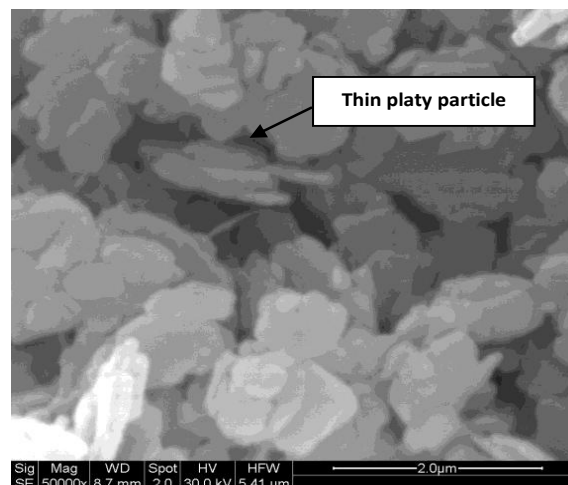


Figure4.SEM micrograph of untreated clay with of 0.5% humic acid.

Figures5 and 6 show a soil structure of specimens with higher humic acid content (i.e. 1.5% and 3.0%). In contrast to Figures 3 and 4, the early stages of the particle disintegration (crumble) of some particles were evident and the occurrence of some cracks was observed in the clay sample with 1.5% humic acid concentration, as shown in Figure5. These cracks became even more apparent for the clay with 3% humic acid content, as can be seen in Fig. 6. The occurrence of cracks on individual particles suggests particle breakage resulting from humic acid obstruction. Such an occurrence typically retards particle flocculation with lime making modification process more difficult later. The results obtained at this stage were important to provide an indication of the prospective behaviour of lime-treated organic clay in the next stage of investigation.

In view of large area of micrograph image, the chemical elements present in each specimen were studied using EDX technique. The results of EDX analysis for specimens with various humic acid contents were shown in earlier Table 1. Based on the EDX results, it shows that as the total amounts of carbon and oxide ions increases, so does the humic acid content. As a result, the amount of pozzolan minerals such as silica and alumina decreases with increasing humic acid. This is because the presence of humic acid elements tends to coat the soil mineral thus preventing them from being detected as reported by Koslanant et al. (2006). This may also pose a problem when organic clay is treated with lime as insufficient amount of pozzolan materials can limit the formation of cementing agents produced during pozzolanic reactions.

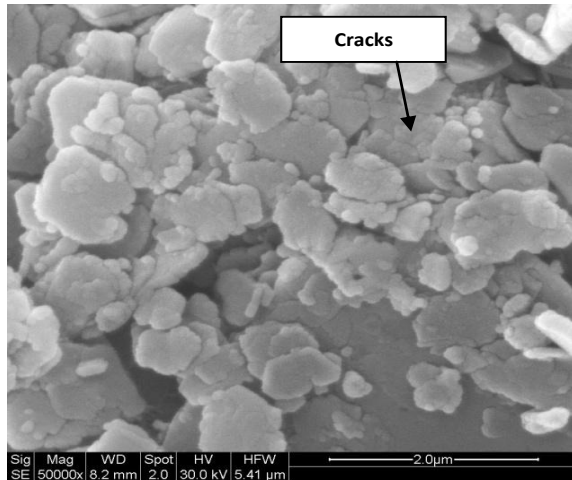


Figure5.SEM micrograph of untreated clay with of 1.5% humic acid content.

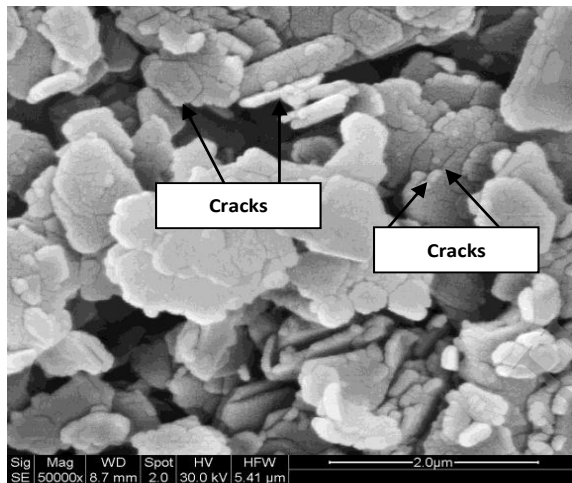


Figure6.SEM micrograph of untreated clay with of 3.0% humic acid content.

4.2. Microstructure of Lime-treated Specimens

A microscopic investigation of the lime-treated samples was carried out. Figure7 shows the image taken for lime-treated inorganic clay. The micrographs of lime-treated organic clays with 0.5%, 1.5% and 3.0% humic acid treated at optimum lime content OLC (5%), after 28 days of curing are shown in Figure8 (a), (b), and (c), respectively. The duration of 28 days curing period represents the stabilisation process. At this stage, the cementation products are expected to form fully in the soil structure in the form of calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH). Although the strength at 28 days was slightly less than that at 7 days, the formations of cementing products were developed in smaller quantities (Al-Mukhtar et al., 2010; MohdYunus et al., 2011 & 2012). The formation of cementing products was also revealed by XRD analysis as

discussed later. As shown Figure7, unlike organic clay, the lime-treated inorganic clay starts to reveal the cementing structure mainly CSH, identified by a fine tubular shape and well knit structure (needle-like form) that bridge the aggregates.

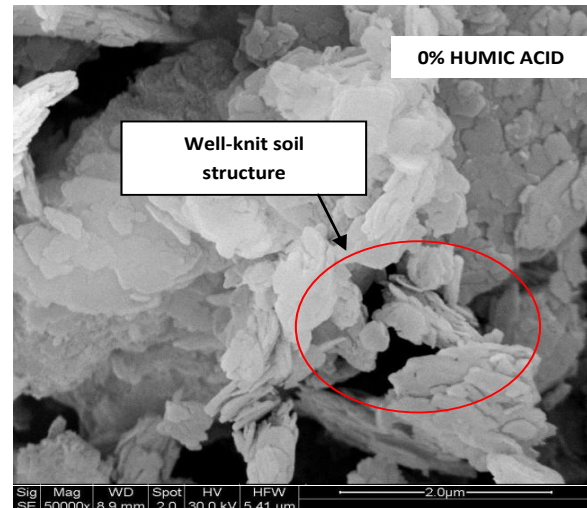
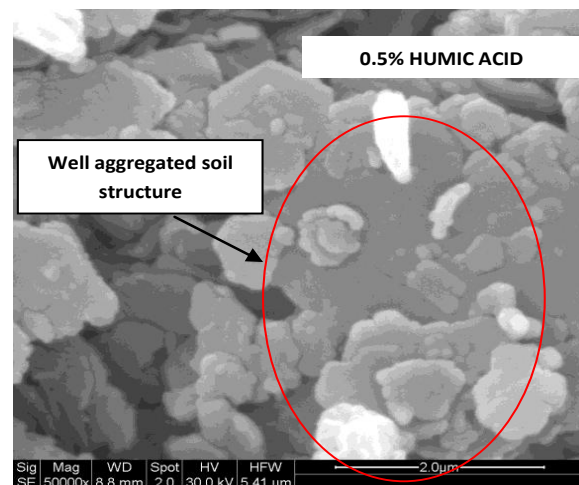


Figure7. The soil structure of lime-treated inorganic clay (0% humic acid) after treatment with 5% lime.

In the case of lime-treated organic clays, images exhibit similar soil structure to that of the untreated specimens (see Figure. 4 - 6). However, the images of lime-treated clay with 0.5% humic acid content taken at the same magnification (Figure8a) revealed well aggregated structure where the particles were clumped to each other to form bigger units. As a result, less pronounced individual plates were observed compared to the untreated soil. Similar observations were reported by Rajasekaran et al. (1997). The appearance of cracks in the untreated clay with 1.5% and 3.0% humic acid improved after the sample was treated with 5% lime, as can be seen in Fig. 8b and c.



(a)

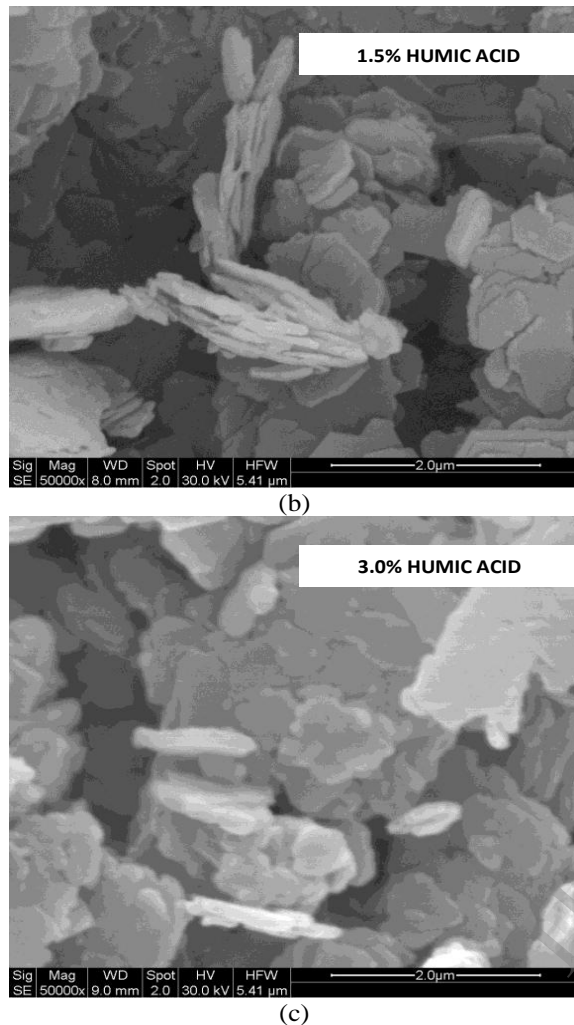


Figure 8. The soil structure of specimens after treatment with 5% lime (a) 0.5%, (b) 1.5% and (c) 3.0% humic acid content.

As the presence of CAH or CSH structures could not be identified from the SEM images of lime-treated organic clays, X-ray diffractometer (XRD) analysis was carried out to determine the amount of chemical compositions with regard to the intensity of cementing materials observed. The difficulties of material to reveal the cementitious structures occur, perhaps because of the small amounts present in the clay. Figure 9 shows a diffraction pattern of lime-treated clay with various humic acid contents. Based on the XRD analysis, the presence of CSH was identified in all lime-treated specimens at different intensity. The presence of CSH was indicated at diffraction angle (2θ) scale of 26.9 in the XRD pattern. However, it was not possible to quantitatively detect CAH as the diffraction pattern of the CAH compounds overlapped with that of the clay minerals (i.e. silica and alumina).

It can be seen from Figure 9, that there was insignificant difference in intensities between lime-

treated specimen with 0% and 0.5% humic acid contents. In contrast, the peak intensity of CSH was reduced when lime-treated clay consisted more than 1.5% humic acid. The XRD results agreed well with UCS tests where the peak intensity of CSH corresponded to the lower amount of humic acid contents and to the higher shear strength (MohdYunus et al., 2011 & 2012).

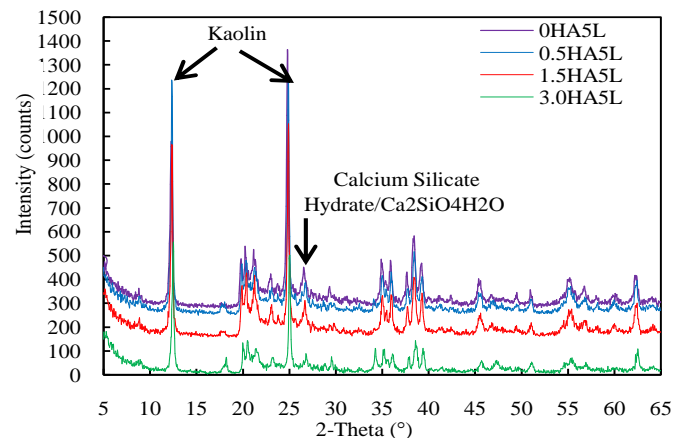


Figure 9. XRD analysis of lime-treated samples.

5. Conclusion

The SEM and XRD analysis carried out in this study showed that, where present, humic acid tended to coat the clay minerals (silica and alumina) and consequently prevented them from being detected by the EDX analysis. The influence of humic acid is also believed to have prevented the lime from adhering to the clay minerals to permit a pozzolanic reaction to take place. A close inspection of the samples revealed cracks on the specimens with higher humic acid content (i.e. 1.5% and 3.0%). The changes in soil structure due to lime stabilisation were only evident visually through flocculation and aggregation, with the effect on cementation hardly identifiable by the SEM images. The SEM images of the lime-treated organic clay revealed the appearance of a well-aggregated microstructure created during stabilization process. Significantly more voids were detected between the aggregates in the clays with higher humic acid contents. However, the appearance of cementing structure could not be observed, thus further verification from XRD analysis was required. Based on XRD analysis, the amount of calcium silicate hydrate (CSH) in lime-treated specimens was observed to increase with decreasing humic acid content. In light of the above mentioned observations, it may be necessary to consider other admixtures (e.g. chloride salts) to mitigate the drawback of humic acid on lime-treated organic clay. However, further research is needed to understand the chemical behaviour of

lime stabilised organic clay in conjunction with salts.

6. References

- Bell, F.G., 1996. Lime stabilization of clay minerals and soils. *Engineering Geology* 42 (4), 223-237.
- Boardman, D., Glendinning, S., Rogers, C.D.F., 2001. Development of stabilisation and solidification in lime-clay mixes. *Geotechnique* 50 (6), 533-543.
- Choquette, M., Andre Bérubé, M., Locat, J., 1987. Mineralogical and microtextural changes associated with lime stabilization of marine clays from Eastern Canada. *Applied Clay Science* 2 (3), 215-232.
- Harris, P., Harvey, O., Sebesta, S., Chikyala, S.R., Puppala, A. and Saride, S. (2009). "Mitigating the effects of organics in stabilized soil." Technical Report No. 0-5540-1, Texas Transportation Institute, USA.
- Huat, B.B., Maaail, K.S., Ahmed Mohamed, T., 2005. Effect of chemical admixtures on the engineering properties of tropical peat soils. *American J. of Applied Sciences* 2 (7), 1113-1120.
- James, R., Kamruzzaman, A.H.M., Haque, A., Wilkinson, A., 2008. Behaviour of lime-slag-treated clay. *Proc. the ICE, Ground Improvement* 161 (4), 207-216.
- Koslanant, S., Onitsuka, K., Negami, T., 2006. Influence of salt additive in lime stabilization on organic clay. *Geotechnical Engineering* 39, 95-101.
- Kumar, A., Walia, B.S., Bajaj, A., 2007. Influence of fly ash, lime, and polyester fibers on compaction and strength properties of expansive soil. *Journal of Materials in Civil Engineering* 19 (3), 242-248.
- Mallela, J., Harold Von Quintus, P.E., Smith, K.L., 2004. Consideration of lime-stabilized layers in mechanistic-empirical pavement design. *The National Lime Association, Arlington, Virginia*.
- MohdYunus, N.Z., Wanatowski, D., Stace, L.R., 2011. Effect of humic acid and salt additives on the behavior of lime-stabilised organic clay. *Second International Conference on Geotechnique, Construction Materials and Environment, Kuala Lumpur, Malaysia, Nov. 14-16, 2012, ISBN: 978-4-9905958-1-4 C3051, 253-256*.
- MohdYunus, N.Z., Wanatowski, D., Stace, L.R., 2012. Effectiveness of Chloride Salts on the Behaviour of Lime-Stabilised Organic Clay. *Int. J. of GEOMATE, Geotec., Const. Mat. & Env., ISSN:2186-2982(P), 2186-2990(O), Japan, Vol. 3, No. 2 (Sl. No. 6), 407- 412*.
- Al-Mukhtar, M., Lasledj, A., Alcover, J-F., 2010. Behaviour and mineralogy changes in lime-treated expansive soil at 20 °C. *Applied Clay Science* 50, 191-198.
- Onitsuka, K., Modmoltin, C., Kouno, M., 2001. Investigation on microstructure and strength of lime and cement stabilized Ariake clay. *Reports of the Faculty of Science and Engineering, Saga* 30 (1), 49-63.
- Petry, T.M., Glazier, E.J., 2004. The effect of organic content on lime treatment of highly expansive clay. *Project Report*.
- Rajasekaran, G., Rao, N., 1997. The microstructure of lime-stabilized marine clay. *Ocean Engineering* 24 (9), 867-875.
- Rogers, C., Roff, T., 1997. Lime modification of clay soils for construction expediency. *Proceedings of ICE, Geotechnical Engineering* 125 (4), 242-249.
- Sakr, M.A., Shahin, M.A., 2009. Utilization of Lime for Stabilizing Soft Clay Soil of High Organic Content. *Geotechnical and Geological Engineering* 27, 105-113.
- Uppal, H.L., Chadda, L.R., 1967. Physico-chemical changes in the lime stabilization of black cotton soil (India). *Engineering Geology* 2 (3), 179-189.
- Zhu, W., Chiu, C.F., Zhang, C.L., Zeng, K., 2009. Effect of humic acid on the behaviour of solidified dredged material. *Canadian Geotechnical Journal* 46 (9), 1093-1099.