UNIVERSITI PUTRA MALAYSIA

EFFECTS OF ACID RAIN ON GEOTECHNICAL PROPERTIES OF TROPICAL RESIDUAL SOILS

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FK 2017 4

EFFECTS OF ACID RAIN ON GEOTECHNICAL PROPERTIES OF TROPICAL RESIDUAL SOILS

By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

January 2017

DEDICATION

I would like to dedicate my PhD thesis to my parents and my husband

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

EFFECTS OF ACID RAIN ON GEOTECHNICAL PROPERTIES OF TROPICAL RESIDUAL SOILS

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January 2017

Chairman : Professor Bujang Kim Huat, PhD
Faculty : Engineering

Acidic deposit that falls to earth from the atmosphere is named acid rain. Sulfur dioxide (SO_2) and oxide of nitrogen (NO_x) are being constantly released as gases into the atmosphere. These oxides react with the rainwater to produce stronger acids and might lower the pH to 4.5 or even 2.0. This research aimed at determining the effect of acid rain on residual soil and kaolinite in the tropical area. Fore types of soils sedimentary residual soil (SRS), igneous residual soil (IRS), primary kaolinite (PK) and secondary kaolinite (SK) with different properties were chosen. Soaking and infiltration methods were employed to simulate the natural environment and reaction of acid rain on the selected soils based on short-term and long-term reaction. For the soaking method, the specimens were kept in the artificial acid rain (AAR) container for 7, 14, 28, and consequently 90 days, while in the infiltration method, the specimens were kept at flux of AAR for 1, 5, 10, and 20 years at different pH levels for both methods. The AAR was prepared by adding certain volume of 0.005M nitric acid (HNO_3) and sulfuric acid (H_2SO_4) to the deionized distilled water. The pH values of the AAR were adjusted to 2, 3, 4, 5, and 5.6. All soils' properties via physico-chemical and mechanical were assessed before and after treatment of specimens with AAR to identify the effect of the AAR on the soils. For the mechanical properties tests, unconfined compressive strength (UCS), consistency limits, optimum moisture content (OMC), maximum dry density (MDD), hydraulic conductivity, and one-dimensional consolidation tests were carried out. Whereas, to examine the effects of AAR on soil chemical mechanism, the microstructural tests were performed using zeta potential (ζ), Atomic adsorption spectroscopy (AAS), X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDX). In soaking method (i.e. short-term), low pH value of AAR changed the characterization of SRS IRS, PK, and SK, and led to an increase in soil strength and maximum dry density (MDD), and reduction in the hydraulic conductivity, Atterberg limits, and optimum moisture content (OMC). In terms of long-term effect of acid rain, the low pH value and high fluxes of AAR changed the characterization of SRS IRS, PK, and SK and led to a reduction in soil strength and MDD, and an increase in the hydraulic conductivity,

Atterberg limits, and OMC, initial void ratio, and Cc of SRS, IRS, PK, and SK. Long-term flux of AAR led to a further increase in compressibility of the studied soils. Regarding the influence of flux of acid rain on the soil properties, the acidic pH level of rain has significant effects on the physico-chemical properties. The effect of acid rain on the properties of soils will become more serious if the rainwater is further acidified due to heavier industrialization.

Key words: Acid rain; Residual soil; Kaolinite; Atterberg limits; Compressive strength; Consolidation; Compaction characteristics; Hydraulic conductivity.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

KESAN HUJAN ACID PADA SIFAT GEOTEKNIKAL TANAH TANAH TROPIK

Oleh

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Deposit berasid yang jatuh ke bumi dari atmosfera dinamakan hujan asid. Sulfur dioksida (SO_2) dan oksida nitrogen (NO_x) sedang sentiasa dikeluarkan sebagai gas ke atmosfera. Ini oksida bertindak balas dengan air hujan untuk menghasilkan asid kuat dan mungkin menurunkan pH 4.5 atau 2.0. Kajian ini bertujuan untuk menentukan kesan hujan asid pada tanah baki dan kaolinites di kawasan tropika. jenis Fore tanah sedimen sisa tanah (SRS), igneus sisa tanah (IRS), kaolinit utama (PK) dan kaolinit menengah (SK) dengan ciri-ciri yang berbeza telah dipilih. Rendaman dan penyusupan kaedah telah digunakan untuk mensimulasikan persekitaran semula jadi dan tindak balas hujan asid di tanah yang dipilih berdasarkan jangka pendek dan tindak balas jangka panjang. Bagi kaedah rendaman, spesimen disimpan di dalam bekas hujan asid tiruan (AAR) selama 7, 14, 28, dan seterusnya 90 hari, manakala dalam kaedah penyusupan, spesimen telah disimpan di fluks AAR untuk 1, 5, 10 , dan 20 tahun pada tahap pH yang berbeza untuk kedua-dua kaedah. The AAR telah disediakan dengan menambah jumlah tertentu 0.005M asid nitrik (HNO_3) dan asid sulfurik (H_2SO_4) untuk air suling yang ternyahion. Nilai pH AAR telah diselaraskan untuk 2, 3, 4, 5, dan 5.6. sifat-sifat semua tanah 'melalui fiziko-kimia dan mekanikal telah dinilai sebelum dan selepas rawatan spesimen dengan AAR untuk mengenal pasti kesan AAR di tanah. Bagi hartanah ujian mekanikal, kekuatan mampatan tak terkurung (UCS), had konsisten, kandungan lembapan optimum (OMC), ketumpatan kering maksimum (MDD), kekonduksian hidraulik, dan ujian pengukuhan dimensi satu- telah dijalankan. Manakala, untuk mengkaji kesan AAR mekanisme kimia tanah, ujian mikrostruktur telah dilakukan dengan menggunakan potensi zeta (ζ), Atomic penjerapan spektroskopi (AAS), X-ray pembelauan (XRD), Fourier berubah spektroskopi inframerah (FTIR), elektron imbasan mikroskop (SEM), dan tenaga serakan X-ray spektroskopi (EDX). Dalam kaedah rendaman (iaitu jangka pendek), nilai pH yang rendah AAR berubah pencirian SRS IRS, PK, dan SK, dan membawa kepada peningkatan dalam kekuatan tanah dan ketumpatan kering maksimum (MDD), dan pengurangan dalam kekonduksian hidraulik, had Atterberg dan kandungan lembapan optimum (OMC). Dari segi kesan jangka panjang hujan asid, nilai pH yang rendah dan fluks tinggi AAR berubah pencirian SRS IRS, PK, dan SK, dan membawa

kepada pengurangan dalam kekuatan tanah dan MDD, dan peningkatan dalam kekonduksian hidraulik, had Atterberg dan OMC, nisbah lompang asal, dan Cc daripada SRS, IRS, PK, dan SK. fluks jangka panjang AAR membawa kepada peningkatan lagi dalam kebolehmampatan tanah dikaji. Mengenai pengaruh fluks hujan asid pada sifat tanah, tahap pH berasid hujan mempunyai kesan yang besar ke atas sifat-sifat fiziko-kimia. Kesan hujan asid kepada sifat-sifat tanah akan menjadi lebih serius jika air hujan itu lebih berasid disebabkan oleh perindustrian yang lebih berat.

ACKNOWLEDGEMENTS

My utmost gratitude goes to God. I would like to express a special thanks to my supervisor Professor Bujang Kim Huat. It was a well rewarding experience to have been under his supervision. I deeply appreciate his patient instructions and continuous support he has given me during my study and research. I am also graceful to my supervisory committee members, Professor Asuri Sridharan, Dr. Afshin Asadi, and Dr. Haslinda Nahazana.

On a personal note, I would especially like to thank my lovely husband Sayed Hessam Bahmani for his kind full supports during the difficult moments of my research and my life and I would like to thank my cobber Samira Jilani Kojouri for her kind supports during the difficult moments of my research. I owe my loving thanks to my parents Ali Bakhshipour and Ashraf Bakhtiary. I am especially thankful to my lovely sister Zahra Bakhshipour and my brothers Ehsan Bakhshipour and Amir Hossein Bakhshipour for their kind, supportive, and valuable helps during my research.

My deep acknowledgment is duly expressed to Professsor Shahrin Ibrahim, Dr Sorraya Hosseini and Dr Hossein Jahangiri for their guidance in chemical parts of my research.

Last but not the least; I am thankful to the Engineering Faculty of University Putra Malaysia and all my friends in geotechnical laboratory. I hope Allah pay back all of their kindness that I have received during all these years.

I certify that a Thesis Examination Committee has met on 9 January 2017 to conduct the final examination of Zeinab Bakhshipour on her thesis entitled "Effects of Acid Rain on Geotechnical Properties of Tropical Residual Soils" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

SO_4^{2-}	Sulfate
NO_3^-	Nitrate
Al_20_3	Aluminum dioxide
Fe_2O_3	Iron dioxide
NaO	Sodium oxide
CaO	Calcium oxide
XRD	X-Ray Diffraction
SEM	Scanning electron microscope
EM	Electrophoretic mobility at actual temperature
Vt	Velocity of the suspending liquid
Dt	Dielectric constant
AAS	Atomic adsorption spectroscopy
SEM	scanning electron microscope
Cc	Compression Index
PK	Primary kaolinite
SK	Secondary kaolinite
SRS	Sedimentary residual soil
IRS	Igneous residual soil
CEC	Cation exchange capacity
Fe	Iron
Al	Aluminum
Si	Silicate
Ca	Calcium

K	Potassium
Na	Sodium
Mg	Magnesium
Fe_2O_3	Iron oxide
Al_2O_3	Aluminum oxide
SiO_2	Sulfur oxide
SO_2	Sulfur dioxide
NO_x	Nitrogen oxides
OH	Hydroxide
H	Hydrogen
H_2SO_4	Sulfuric acid
HNO_3	Nitric acid
BSI	British Standard Classification
a.u.	Arbitrary unit
ASTM	American Society for Testing and Material
BS	British Standard
USCS	Unified Soil Classification System
CL	low medium plasticity
MH	Elastic Silt
Rave	Stands for annual average precipitation
A	Stands for the cross sectional area of the specimen
AAR	Artificial acid rain
kg/m^3	Kilograms per Cubic Meter
kN/m^3	Kilonewtons per Cubic Meter
m	Meter

cm	Centimeter
mm	Millimeter
µm	Micrometer
I	Illite
K	Kaolinite
G	Goethite
Q	Quartz
H	Hematite
K-Feldspar	Kaolinite Feldspar
S	Smectite
Mg/m3	Milligram per Cubic Meter
kPa	Kilo Pascal

LIST OF SYMBOLS

LL	Liquid limit	%
PL	Plastic limit	%
PI	Plasticity Index	%
SL	Shrinkage limit	
W	Natural water content	%
G_S	Specific gravity	
MDD	Maximum dry density	mg/m^3
OMC	Optimum moisture content	%
ζ	Zeta potential	(mV)
π	Constant	
UCS	Unconfined compressive strength	kPa
strain	Compressive strain	%
e	void ratio	
$\sigma'v$	Effective vertical stress	
m_1	mass of density bottle including stopper	g
m_2	mass of density bottle, stopper and oven dried soil	g
m_3	mass of density	g
m_4	mass of density bottle, stopper and distilled water	g
p_d	Dry density	g/cm^3
p_w	Wet density	g/cm^3
m_w	Wet sample	g
D	The mean diameter of the specimen	cm
L	The mean length of the soil specimen	cm

k	Hydraulic conductivity	m/s
LS	Linear shrinkage	%
A	cross section area	m^2
L	length of sample	m
Φ	Porosity	%

CHAPTER 1

INTRODUCTION

1.1 General

Research conducted over the past few decades indicates that changes in pore water chemistry may significantly alter the geotechnical properties of soils (Bolt, 1956, Mitchell, 1960, Rosenqvist, 1959, Santamarina et al., 2002).Geotechnical practices indicate that engineering structures built on such soils can experience significant deformation due to changes in the soil's structure (Sridharan et al., 1981). Therefore, the engineering properties of soil have received special consideration by researchers. One of the most important and obvious sources of soil pollution is acid rain. The major sources of acid rain are sulphur dioxide (SO_2) and nitrogen oxides (NO_x)(Streets and Waldhoff, 2000). These oxides react with rain water to produce stronger acids with a low pH of 4.5, or even 3.0. The engineering properties of soils are significantly influenced by the chemical properties of the soil and is termed "chemical-mechanical coupling"(Santamarina et al., 2002). The acid rain and its annual rate in the various areas cause to increase weathering rate in the soils (Denman et al., 2007). It is true that the weathering factor is the main fact which owing to the formation of residual soils in the tropical areas (Kato and Akimoto, 1992). The major types of soil in Malaysia as a tropical area are residual soils (Galloway, 1989).

In this study two common types of residual soil, including sedimentary residual soil and igneous residual soil were chosen. It is noticeable that in almost all of the tropical residual soils in Malaysia, kaolinite is one of the dominating clay minerals (Tan, 2009). Kaolinite is classified into two broad categories which is called primary and secondary (Bignell et al., 2002). The primary kaolinite or residual kaolin originates from in situ alteration of rocks by hot fluids, which permeate mainly in pegmatite. Generally primary kaolinite has not been altered chemically since its deposition and crystallization as a result of large-scale geological processes (Bolland et al., 1976). In addition, the secondary minerals from the decomposition and restructuring of primary minerals or from precipitation reactions concerning chemical constituents of primary kaolinite released during dissolution (Bloodworth et al., 1993, Bolland et al., 1976). Secondary kaolinite is generally characterized by smaller particle size, because the particle size of primary kaolinite is decreased during weathering and release of soluble materials (Bloodworth et al., 1993, Scorzelli et al., 2008b). Based on the existing literature, it can be concluded that the following chemical and physical processes might describe the effect of acid rain on soil (Benna et al., 2002, Jozefaciuk and Bowanko, 2002): (I) Dissolution and leaching of cations or anions from soil, based on their solubility at different pH values; (II) Changes in surface electrical properties in the colloidal fraction of soil; (III) Absorption of anions in acid rain such as SO_4^{2-}, NO_3^{2-}, and CO_3^{2-} in the soil environment; and (IV) Changes in diffuse double layer of the clay fraction due to the ion exchange and consequent changes in the van der Waals forces acting between the clay particles, which may result in a change in engineering properties of soil affected by acid rain.

1.2 Statement of the Problem

One of the most important and sources of soil pollution is acid rain. Geotechnical properties can be changed under effect of acid rain. Moreover, increasing urbanisation and industrialisation in developing countries, such as Malaysia, have extended the geographical occurrence of acid rain. Malaysia is one of the areas that have undergone to experience the effects of acid rain. The major types of soil in Malaysia as a tropical area are residual soils. It is noticeable that among all of the tropical residual soils in Malaysia, kaolinite is one of the dominating clay minerals. The reaction of variety of soils and minerals affected by acid rain is different. The literature review show that the effects of acid rain on physico-chemical and engineering properties of soil could vary due to the complexity of mineral composition of the parent soil and chemical properties of the pore fluid. However, there is still a lack of comprehensive knowledge on the physical and chemical mechanisms of influence of acid rain on the minerals in tropical area. It should be noted that although the effect of each minerals on the properties of clay in an acidic medium seems to be well understood, whereas the behaviour of different kinds of kaolinite in tropical area still remains unclear. The primary aim of this study is to determine the effects of acid rain in tropical area on two common types of residual soils and different kaolinites.

1.3 Objectives

The objectives of this study are:

I. To investigate short term effects of acid rain on geotechnical properties of sedimentary residual soil, igneous residual soil, primary kaolinite, and secondary kaolinite.

II. To investigate long term effects of acid rain on geotechnical properties of sedimentary residual soil, igneous residual soil, primary kaolinite, and secondary kaolinite.

III. To determine the underlying mechanisms controlling the effect of acid rain on the sedimentary residual soil, igneous residual soil, primary kaolinite, and secondary kaolinite.

1.4 Scope of Study

The purpose of this research is to observe the changing in tropical residual natural soils and clay minerals. The scopes and limitations of the research is including of the sedimentary residual soil (SRS) and igneous residual soil (IRS) were selected from Batu Cave and Taman Ukay Perdana respectively in Kuala Lumpur, Malaysia and primary kaolinite (PK) and secondary kaolinite (SK). Moreover, in this research the short and long term effect of acid rain with choosing two methods of soaking and infiltration method used to investigate the reality event.The strength and compressibility evaluation tests for the samples are UCS test and consolidation test respectively. In addition, the maximum flux of artificial acid rain used for the strength evaluations of samples are 90 days and 20 years in soaking and infiltration method

respectively. Furthermore, the chemical properties of acid rain on soils and kaolinites are evaluated by X-ray diffraction (XRD), scanning electron microscopy (SEM), Scanning Electron Microscopy (EDX), zeta potential, and atomic adsorption spectroscopy (AAS).

1.5 Thesis Layout

The chapters of the thesis are organized as follows:

Chapter 2 presents the literature review on acid rain and deposition, history of acid rain and the potential of acid rain in different country. This chapter also includes the principle of residual soil and clay minerals that include of primary and secondary kaolinite and the most important clay minerals of residual soils. Furthermore, this chapter presents the effect of acid rain on physical and engineering properties of different soils.

Chapter 3 discusses the sampling location of soils and minerals, moreover explained the geotechnical test, the preparation of acid rain exposure, short and long term method which include of soaking and infiltration methods. This chapter also describes the microstructure analysis of soils as affected by acid rain at different time and pH.

Chapter 4 describes the effect of acid rain on residual soils and kaolinites at short and long term effect at different pH value on some engineering properties of soil. The study evaluated the microstructure analysis of soils and minerals by effect of acid rain at long at short term effect. Consequently the proposed mechanism under effect of acid rain is explained.

Chapter 5 presents the conclusions arrived from this study and recommendations for future research.

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