

**FACTORS AFFECTING CHARGE
CHARACTERISTICS AND BUFFERING
CAPACITY OF SOME SOILS OF EGYPT**

By

MOHAMED SALAH KOTB RAMADAN

**B.Sc. Agric. Sci. (Soil), Fac. Agric., Cairo Univ., 2000
M.Sc. Agric. Sci. (Soil), Fac. Agric., Cairo Univ., 2006**

THESIS

**Submitted in Partial Fulfillment of the
Requirements for the Degree of**

DOCTOR OF PHILOSOPHY

In

**Agricultural Science
(Soil Science)**

**Department of Soil Science
Faculty of Agriculture
Cairo University
EGYPT**

2011

APPROVAL SHEET

**FACTORS AFFECTING CHARGE
CHARACTERISTICS AND BUFFERING
CAPACITY OF SOME SOILS OF EGYPT**

**Ph.D. Thesis
In
Agric. Sci. (Soil Science)**

By

MOHAMED SALAH KOTB RAMADAN

B.Sc. Agric. Sci. (Soil), Fac. Agric., Cairo Univ., 2000

M.Sc. Agric. Sci. (Soil), Fac. Agric., Cairo Univ., 2006

APPROVAL COMMITTEE

Dr. EID MORSY KHALED
Professor of Soil Sciences, Fac. Agric., Ain Shams University

Dr. MAHER ABD EL-MOHSEN ABD EL-HAMID
Professor of Soil Sciences, Fac. Agric., Cairo University

Dr. YEHIA ARAFA AHMED NASR.....
Associate Professor of Soil Sciences, Fac. Agric., Cairo University

Dr. REDA RAGAB MOHAMED SHAHIN
Professor of Soil Sciences, Fac. Agric., Cairo University

Date: 14 /12/ 2011

SUPERVISION SHEET

**FACTORS AFFECTING CHARGE
CHARACTERISTICS AND BUFFERING
CAPACITY OF SOME SOILS OF EGYPT**

**Ph.D. Thesis
In
Agric. Sci. (Soil Science)**

By

MOHAMED SALAH KOTB RAMADAN

B.Sc. Agric. Sci. (Soil), Fac. Agric., Cairo Univ., 2000

M.Sc. Agric. Sci. (Soil), Fac. Agric., Cairo Univ., 2006

SUPERVISION COMMITTEE

Dr. REDA RAGAB MOHAMED SHAHIN
Professor of Soil Sciences, Fac. Agric., Cairo University

Dr. YEHIA ARAFA NASR
Associate Professor of Soil Sciences, Fac. Agric., Cairo University

DEDICATION

I dedicate this work to whom my heartfelt thanks; to my wife for her patience and support, as well as to my parents for all the help they lovely offered along the period of my post graduation.

ACKNOWLEDGEMENT

At the first, I thank Allah who made me able to supplement this work.

*Then, I would like to express my sincere acknowledgement and deepest appreciation to **Dr. Reda Ragab Mohamed Shahin**, Prof. of Soil Science, Faculty of Agriculture, Cairo University, for his sincere supervision, suggesting the problem, valuable scientific assistance, encouragement, continuous guidance and constructive criticism which made the completion of this work possible. Also, my sincere thanks go to **Dr. Yehia Arafa**, Associate Professor of Soil science, Faculty of Agriculture, Cairo University, for his useful advices, continuous encouragement and simplifying all obstacles I have faced. I do appreciate the support and encouragement given by all, I do not remember, helped me during all different stages of my research.*

Grateful appreciation is also extended to all staff members of Soil Department, Faculty of Agriculture, Cairo University.

Special deep appreciation is given to my father, my mother, my wife and brothers.

CONTENTS

	Page
INTRODUCTION	1
REVIEW OF LITERATURE	3
1. Charge development in soils.....	3
2. Surface Charge Balance.....	6
3. Points of Zero Charge.....	10
4. Nature of soils with variable charge.....	14
5. Chemistry of soil charge.....	17
6. Effect of soil components on charge characteristics.....	26
7. P-oxyanion adsorption impact on charge characteristics.....	31
8. pH-Buffering Capacity.....	33
MATERIALS AND METHODS	37
RESULT AND DISCUSSION	51
1. Charge characteristics of synthetic soil components.....	51
a. Potentiometric titration curves of synthetic soil components.....	51
b. Ion adsorption curves of synthetic soil components.....	55
c. Positive and negative charges of synthetic coatings.....	62
d. Zero point of charge coated sands.....	70
e. Infra-Red spectra of synthetic soil components.....	74
f. Deprotonation constants of sand synthetic coatings.....	82
2. Charge characteristics of soil samples.....	88
a. Soil Potentiometric titration curves.....	88
b. Ion adsorption curves.....	102
c. Dissociation constants (pK_a) of the surface active groups in soils.....	115
3. Phosphate adsorption isotherms of the alluvial and calcareous soils.....	125
4. Buffering capacity of the different soils components.....	167
5. Buffering capacity of soils.....	173
SUMMARY	191
REFFERENCES	201
APPENDICES	221
ARABIC SUMMARY	

INTRODUCTION

The soil environment remains one of the most complex and poorly understood research frontiers in ecology. The specialization required to measure unseen processes that occur on a wide range of spatial and temporal scales has led to the partitioning of soil scientific research across several disciplines and scales. One of the unseen processes is the dynamic nature of surface charges of soil colloids. Dramatic changes in the surface charge can be caused by changes in soil nanoparticle coatings, surface treatment, and the chemical characteristics of the soil media especially soil acidity (pH may drop by 2-3 units in the root zone, Rao *et al.* 2002).

Type and intensity of negative and positive charges have great scientific and practical importance in soil–plant nutrition relationships; sorption and desorption of ions; buffering capacity, mobility and leachability of ions, soil dispersion-flocculation behavior; and transformation of agro-chemicals; animal municipal and industrial waste to soil. There are two types of charges in soil, permanent and variable charges. The proportion of each type is of vital importance in controlling the electrochemical properties of any soil. Soils with heterogeneous charge systems confer a quite interesting and much more complex pattern with respect to soil physical and chemical behavior. The use of new and advanced laboratory techniques over the last few years have contributed to a better understanding of chemical behavior of variable charge components in soils.

The charge characteristics of soils in Egypt were untouched and unrevealed throughout the literature. The present study is an attempt to figure out the magnitude of each charge type and points of zero charges for soil samples from typical soils of Egypt. Potentiometric titration, ion adsorption and pH-CEC curves were used to calculate the different charge parameters. However, the main objectives of the present study are to:

1. Study the charge characteristics of synthetic soil components; organic matter, carbonate and amorphous material using incubation experiments.
2. Quantify the charge characteristics of selected alluvial (Torriorthents and Torrifluvents), calcareous (Calciorthids) soils of Egypt.
3. Determine P-oxyanion sorption isotherm in the studied soils and its relation to charge properties.
4. Determine the quantitative relationships between the percent of synthetic soil components and the different charge parameters.
5. Measure soil buffering capacity as affected by pH and its relation to synthetic soil components.

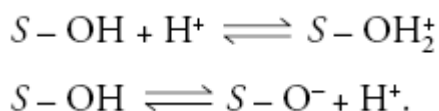
REVIEW OF LITERATURE

Particles of organic and mineral soils can exhibit two types of charges, permanent or constant charge and variable or pH-dependent charges. In most soils there is a combination of constant and variable charge. Constant charge is invariant with soil pH and results from isomorphous substitution and structure imperfections. Therefore, this component of charge was developed during the genesis and formation of soil minerals. Examples of inorganic soil components that exhibit constant charge are smectite, vermiculite, mica, and chlorite. The variable charge component in soils changes with pH due to protonation and deprotonation of functional groups on inorganic soil minerals such as kaolinite, amorphous materials, metal oxides, oxyhydroxides, hydroxides, layer silicates coated with metal oxides and soil organic matter.

1. Charge development in soils

Surface functional groups in soil particles play a significant role in adsorption processes. A surface functional group is “a chemically reactive molecular unit bound into the structure of a solid at its periphery such that the reactive components of the unit can be bathed by a fluid” (Sposito, 1989). Surface functional groups can be organic (e.g., carboxyl, carbonyl, phenolic) or inorganic molecular units. The major inorganic surface functional groups in soils are the siloxane surface groups associated with the plane of oxygen atoms bound to the

silica tetrahedral layer of a phyllosilicate ($\equiv\text{Si-O}$). The hydroxyl group associated with silica is called ‘silanol’ ($\equiv\text{Si-OH}$) and locates on the edges of phyllosilicate minerals. The basal plan of 1:1 minerals (Kaolinite and halloysite), amorphous materials, and metal oxides, oxyhydroxides, and hydroxides are considered as hydroxylated surfaces (Chorover, 2002). The surface functional groups can be protonated or deprotonated by adsorption of H^+ and OH^- , respectively, as shown below:

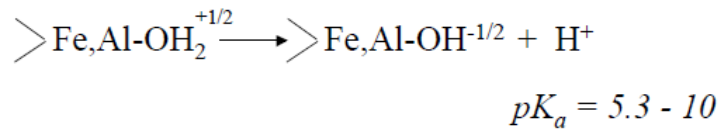
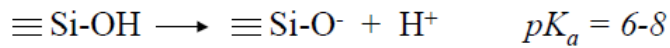


Here the Lewis acids are denoted by S and the deprotonated surface hydroxyls are Lewis bases. The water molecule is unstable and can be exchanged for an inorganic or organic anion (Lewis base or ligand) in the solution, which then bonds to the metal cation. This process is called ligand exchange (Stumm, 1987, 1992).

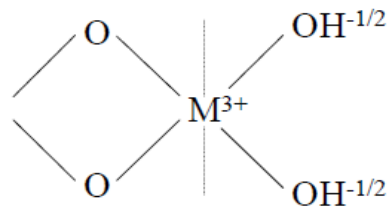
The Lewis acid sites are present not only on metal oxides (i.e. on the edges of gibbsite or goethite), but also on the edges of clay minerals (i.e. kaolinite). At the edge of the octahedral sheet, OH groups are singly coordinated to Al^{3+} , and at the edge of the tetrahedral sheet they are singly coordinated to Si^{4+} . The OH groups coordinated to Si^{4+} dissociate only protons; however, the OH coordinated to Al^{3+} dissociate and bind protons. These edge OH groups are called silanol (SiOH) and aluminol (AlOH), respectively (Sposito, 1989; Stumm, 1992). Which showed as follows:

- Edge Charge - Layer Silicates

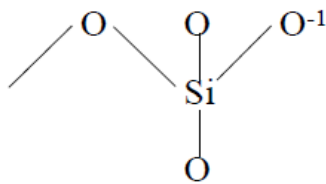
- Edges where neither Al/Si are fully coordinated with oxygen



In addition the charge development could be on oxygen or hydroxyl exposed on the surfaces as follow:



Edge pH dependent terminal OH



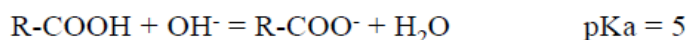
Edge pH dependent terminal O

The surface charge of soil mineral particles is expected to increase as the more strongly acidic silanol sites associated with metastable silicates are depleted from the soil. The abundance of the weakly acidic surface OH-groups of ferrol (=Fe-OH), and aluminol (=Al-OH) also increase soil pH (Chorover *et al.* 2004).

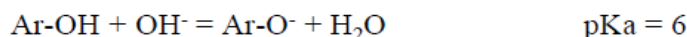
Soil organic matter is critically important to soil charges, since it contains a diverse mixture of molecules and associated functional groups varying in acidity (Cooke *et al.* 2008). The charge is developed in soil organic matter through the dissociation of the dominant groups (i.e. carboxyl, hydroxyl and phenol). Each group dissociates at a certain pH value as follows:

- **Organic matter**

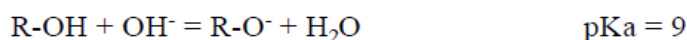
- Carboxyl group



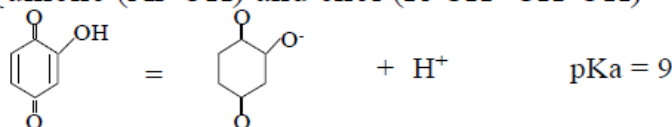
- Phenolic Group



- Linear/aromatic alcoholic groups



- Quinone (Ar-OH) and enol (R-CH=CH-OH)



Smith *et al.* (2004) stated that the susceptibility of any functional group to the dissociation is differed according to its geometrical orientation in the organic structure. Therefore, a specific functional group could have more than one pH value that stimulates its dissociation (Campitelli *et al.* 2003).

2. Surface Charge Balance

Measurements of surface charge for soil particles must account explicitly for the diversity and conditional nature of the principal components that contribute to this quantity. Sposito (1989) stated that

the four components of surface charge contribute to the net total particle surface-charge density (σ_p) are: a. the net permanent structural surface-charge density (σ_0) that is created by isomorphic substitutions in soil minerals. These substitutions occur in both primary and secondary minerals, but they produce significant (negative) surface charge only in the 2:1 layer-type aluminosilicates (Dixon and Weed, 1989), b. the net proton surface-charge density (σ_H) is created by differences between the moles of protons and the moles of hydroxide ions complexed by surface functional groups. c. the net inner-sphere complex surface-charge density (σ_{is}) results from the net total charge of ions, other than H^+ and OH^- , which are bound into inner-sphere surface coordination, d. the net outer-sphere complex surface-charge density (σ_{os}) results from the net total charge of ions, other than H^+ and OH^- , which are bound into outer-sphere surface coordination. The net total particle surface charge (σ_p), is the sum of these four components (Sposito, 1989):

$$\sigma_p = \sigma_0 + \sigma_H + \sigma_{IS} + \sigma_{os} \quad (1)$$

Where:

σ_p = Particle surface charge

σ_0 = Structural charge

σ_H = Net proton charge

σ_{IS} = Inner-sphere charge

σ_{OS} = outer-sphere charge

All the charge components are measured as moles of charge per kilogram (mol_c/kg).

If σ_p is non-zero, it must be balanced by the diffuse layer surface-charge (σ_D) which is equal in magnitude, but opposite in sign. The law of surface charge balance may then be written as:

$$\sigma_P = - \sigma_D \quad (2)$$

Ions contributing to σ_{OS} are distinguished from those contributing to σ_{IS} or σ_H by their more extensive solvation and shorter residence time as adsorbed species (Sposito, 1992). For complex adsorbents, including tropical soils, surface charge is likely to be distributed unequally among the many solid phases present because of differences in structural charge, surface site density, and specific surface area. The right side of Equation (1) indicates the contributions of both permanent (σ_0) and conditional (σ_H , σ_{IS} , σ_{OS}) components to particle surface charge. The value of σ_0 is dependent only upon the composition and structure of solid phases while the values of the remaining components depend upon the nature of both the solid and solution phases.

The net charge of ions (excluding H^+ and OH^-) adsorbed into surface complexes and the diffuse ion swarm is given by the surface excess of cation (q_+) minus anion (q_-) charge (Δq , $\text{mol}_c \text{ kg}^{-1}$):

$$\Delta q = q_+ - q_- = \sigma_{IS} + \sigma_{OS} + \sigma_D \quad (3)$$

The surface charge balance requires that the intrinsic charge of soil particles, σ_{in} , including that resulting from both isomorphic substitutions (permanent charge) and proton adsorption (variable charge) must be balanced by adsorption from solution of background cation and anion:

$$\sigma_{in} = \sigma_0 + \sigma_H = - \Delta q \quad (4)$$

These surface charge components must be measured independently to assess conformation of the data to Eqn. 4 (Chorover and Sposito, 1995 and Chorover, 2002). This is particularly important in whole soils comprising admixtures of permanent charge minerals

and organic matter where side reactions can diminish the accuracy of charge measurements. Adsorption and dissolution reactions both consume aqueous H^+ or OH^- ; therefore, proton titration data must account for the stoichiometry of dissolution side reactions. Furthermore, readsorption of charged dissolution products (e.g., Al^{3+} ions) can impact the surface excess of index ions used to measure adsorbed ion charge (Skyllberg and Borggaard, 1998 and Chorover *et al.* 2004).

Phillips and Sheehan (2005) studied the surface charge characteristics of 6 soils, with contrasting chemical and physical properties, using charge balance principles. The presence and magnitude of permanent negative surface charge was largely dependent on clay mineralogy. All soils displayed increasing negative surface charge density and consequently cation exchange with increasing pH. The magnitude of increase for any particular soil was dependent on the type and amount of colloids exhibiting variable surface charge. The increased negative surface charge was attributed to the ionization of functional groups on organic matter, hydrous Fe and Al oxides, and edge sites of kaolinite and smectite.

Temperate -zone soils, containing large quantities of 2:1 layer-type clay minerals, have been modeled as permanent-charge systems (Bolt, 1982) whereas the highly weathered soils of the humid tropics, comprising predominantly kaolinite, iron, and aluminum oxides, and quartz, have been modeled as conditional charge systems (Singh and Uehara, 1986).