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Influence of Calcium Carbonate Content on Electrical Charges Distribution of Calcareous Soils Surfaces

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FOUR clay minerals were identified in some clay fraction separated from three calcareous soils using x-ray diffraction analysis. Electrophoretic mobility V_{ei} of these fractions was determined at different pH values and $CaCO_3$ contents. Zeta potential (ζ) was computed from V_{ei} values. The charge density was calculated through the cation exchange capacity and the surface area of the soil. The distribution of charges in the electrical double layer of these clay fractions was changed due to their $CaCO_3$ contents, and pH. Zeta potential was more pronouncing at lower $CaCO_3$ content. The specific adsorption charges (σ_1) for the three soils were higher than the nonspecific adsorption charges (σ_2) at the lower content of $CaCO_3$. This revealed that as $CaCO_3$ content decreased the charge density increased.

Keywords: X-ray diffraction, Zeta potential, Charge density and Calcium carbonate.

Some clays exhibit high negative charges due to substitution of lower valency cations instead of higher valency cations within normally neutral crystals. This process is referred to isomorphous substitution. The lower valency of the substituting cation results in a residual negative charge, which must be balanced by a cation external to the layer unit, either on its edge or in the interlayer surfaces. Additional negatively charged adsorptive sites occur on the edges of clay minerals, as well as on humus, allophane, and iron and aluminum hydroxides. Because these charges are dependent on soil pH, they are termed variable or pH-dependent, compared to the more permanent charges resulting from isomorphous substitution (Brady & Weil, 1999). One mechanism of pH-dependent charge is associated with the hydroxyl (OH^-) groups on the edges and surfaces of the inorganic and organic colloids.

Inorganic colloids with pH dependent charge include 1:1 clays and Fe and Al hydrous oxides. Under moderately acid conditions, there is little or no charge on these colloids, but as the pH increases, the hydrogen dissociates, reacting with OH^- ions in the soil solution to form water, and resulting in a negative charge.

These reactions are reversible. As the pH increases, the negative charge on the particle surfaces increases, as the pH is lowered, the negative charge is reduced.

The most important physical characteristic of an electrified interface is its surface charge density. Because the reactive solid surfaces in soil are heterogeneous, the concept of surface charge density for them is pluralistic, not monotypic. The objectives of this work are to:

1. Identify the clay mineral types found in calcareous soils.
2. Determine the charge density of the calcareous soil surface.
3. Study the effect of soil calcium carbonate content on the charge density as a function to pH.

Material and Methods

Preparing soil samples for electrical properties determination and X-ray diffraction analysis

Determination of electrical properties needs some specific treatments for soil samples such as:

a. Separation of fine particle fractions

Fine particles of calcareous soils, less than 1 micron in effective diameter, were separated after suspending about 0.5 Kg of each soil in 3 liters of water and decanting the particles that are suspended above the 10 cm depth after 12 hr as calculated using Stocks law for sedimentation. The clay particles collected by this method were about 1 to 2 g for each soil.

b. Removal of carbonates and soluble salts

The carbonates commonly encountered in calcareous soils are those of calcium and magnesium. The presence of carbonates increases the complexity of X-ray diffraction analysis. Cation exchange capacity and surface area measurements can be made more meaningful through removal of carbonates and soluble salts. So, removal of carbonates and soluble salts was done using the following procedure:

Reagents: sodium acetate 1N (136 g/l) adjusted to pH 5.0 with acetic acid.

Procedure: about 500 g of the soil sample, ground to pass a 2-mm sieve was placed into a conical flask. Several hundred milliliters of Na-acetate buffer solution were added, depending on the size of the sample. By heating to 60-80 ° the bubbles of CO_2 will be released (the time required for dissolution of carbonates is dependent upon particle size, type of carbonates, and sample size). When the bubbles of CO_2 are no longer evident it means that carbonates have been removed (Page, 1982).

Zeta potential measurements

Zeta potential is the electric potential in the double layer at the interface between particles, which move in an electric field and the surrounding liquid.

For clay mineral particles, Von Smoluchowiski's equation is most commonly used to convert electrophoretic mobility, to zeta potential, ζ (Instruction Manual, 1971 and Olivier & Sennett, 1967).

$$V_{el} = \epsilon \zeta E / 4 \pi \eta \quad [1]$$

Where:
V_{el}: electrophoretic velocity
ϵ: dielectric constant
E: Applied electrical field
η: viscosity of the medium
ζ: zeta potential

The zeta potential of the clay fraction suspensions with different $CaCO_3$ percentage was determined by measuring the electrophoretic mobility using a micro electrophoresis apparatus (zeta meter Inc. New York, USA).

Determination of specific surface area

The specific surface area (S) of a powdered sample can be defined as the ratio of the total area of a substance to its weight:

$$S = \sum A_i / \sum W_i \qquad [2]$$

where A_i is the surface area of an individual particle and W_i is its weight. $\sum A_i$ and $\sum W_i$ represent the corresponding quantities calculated for the entire sample. Specific surface areas for 5 soil samples were determined by Permaran apparatus (Research Laboratory, Tapiola Finland).

Calculation of charge density and surface potential

The charge density was calculated according to the following formula depending on the CEC and surface area:

$$\sigma = CEC\,(96500)/S \qquad [3]$$

where, σ refers to total surface charge density esu/cm^2 (electrostatic unit per cm^2) surface, CEC is cation exchange capacity meq/100 g soil, S refers to surface area and the number 96500 represents Faraday value.

Then the surface potential was calculated according to the following formula:

$$\sigma_2 = (n \epsilon k T / \pi)^{1/2} \sinh (\nu e \Phi_0 / 2 kT) \qquad [4]$$

Where:
n: local ion concentrations in number of ions/cm^3; n = normality x 10^{-3} x Avogadro's number (6.02 x 10^{23}).
ϵ: the dielectric constant of the medium.
kT: Boltzman constant x absolute temperature = 4 x 10^{-14} erg at room temperature.
Φ_0 : Surface potential ; $z = \nu e \Phi_0 / kT$,
ν: valence of ion
e: elementary charge = 4.8 x10^{-10} esu.

X-ray diffraction

X-ray diffraction techniques were developed to identify soil colloids, because of their small size, and these methods have been dramatically successful in their application to clay minerals (Norrish, 1975). X-ray diffraction analysis of the clay fraction was performed using a "Shimadzu-XD-3" diffractometer; consisting of a generator, X-ray spectrometer and a counting/recording system. A monochromatic Cu-kα X-ray beam; with a wavelength of 1.542 A° was obtained using a copper target and a nickel filter. Oriented aggregates were obtained by spreading the suspensions on glass slides by means of a dropper and drying in air and inserted in the path of the X-ray beam by mounting it in the center of the goniometer. The intensity of the diffracted ray was recorded as a function of the diffraction angel, 2θ.

Results and Discussion

X-ray diffraction

The examination of the clay minerals using x-ray diffraction analysis revealed the presence of five clay minerals (mica, illite, vermiculite, and kaolinite) kaolinite was the dominant mineral. Figure 1 and Table 1 are representing the x-ray diffraction patterns and types of clay minerals found in the used calcareous soil. Kaolinite is the most common type of 1:1 type clay. The 1:1 units are bonded together by hydrogen bonding between hydroxyl groups, thus there is no interlayer surface area, and kaolinite does not swell with the addition of water. There is also little substitution within the tetrahedral or octahedral layers, resulting in a low charge deficit. Kaolinite contains more surface hydroxyl groups than other silicate clays, and is considered to be primarily responsible for anion exchange in temperate or arid region soils. Fine-grained mica possesses 2:1 structure, which is tightly bonded by potassium bridges. Fine-grained mica, therefore, does not swell in water, and most of its charge is neutralized by potassium ions. Fine-grained mica does not exhibit large potentials for shrinking, swelling, and plasticity. Fine-grained micas are expected to exhibit minimal interactions with waste constituents present in soil systems. Vermiculite, considered a limited-expansion clay mineral, is similar to the fine-grained micas, except that potassium is not present. Vermiculite usually has hydrated magnesium (Mg^{2+}) or calcium (Ca^{2+}) in the interlayer neutralizing the charges and acting as bridges to hold the units together. The degree of swelling is less than that of the smectites but more than kaolinite. From Table 1 most of clay minerals constituents are mainly low in surface area and cation exchange capacity. For that reason the surface area and cation exchange capacity of the studied soils arc low as presented in Table 2 and 3 comparing with the alluvial soils.

TABLE 1. Clay minerals found in the used calcareous soil using X-ray diffraction .

Spacing (A°)	Mineral
10.2	Illite
9.24	Mica
10.2	Atapolgite
7.58	Kaolinite

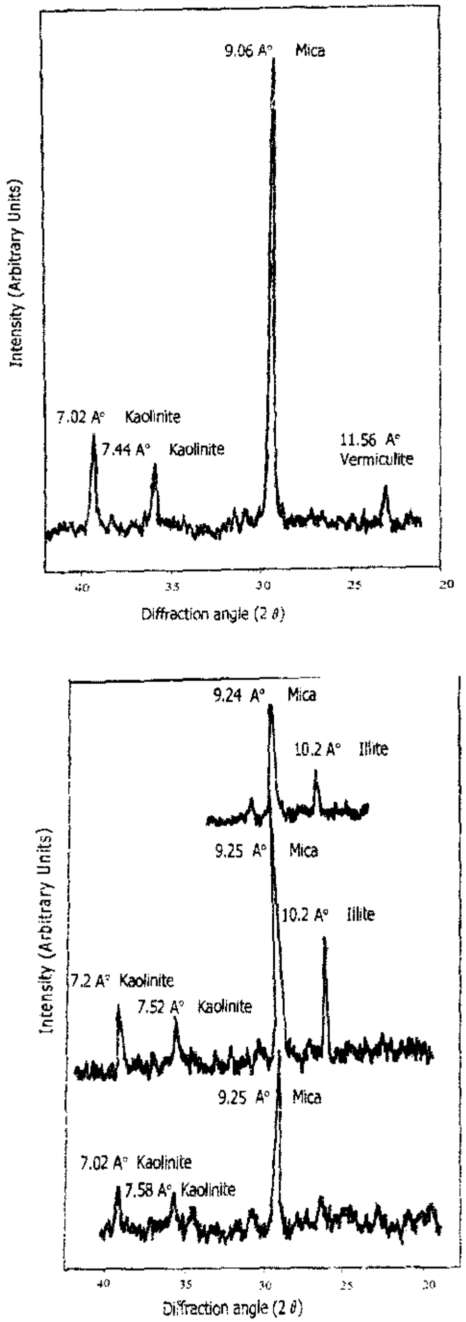

Fig. 1. X-ray diffraction patters.

TABLE 2. Charge distribution of some calcareous soils before removal of $CaCO_3$ at different pH values.

Soil No.	pH	S (m^2/g)	CEC meq/100 soil	$CaCO_3$ %	n Ions/cm^3	ϕ_o mv	ζ mv	σ_1 (esu/cm^2)	σ_2 (esu/cm^2)	σ Total (esu/cm^2)
1	8.3	4.95	7.20	33.1	1.56×10^{18}	1100.0	Zero	38×10^3	Zero	38×10^3
	9.3				1.95×10^{18}	1095.0	28.0	29×10^3	11×10^3	40×10^3
	10.0				8.6×10^{17}	1117.5	33.0	34×10^3	7.0×10^3	41×10^3
	10 5				9.22×10^{17}	1120.1	28.0	38.5×10^3	7.5×10^3	46×10^3
	11.0				8.72×10^{17}	1120.0	42.0	40.5×10^3	7.5×10^3	48×10^3
2	8.3	5.69	4.60	53	1.56×10^{18}	1095.0	14.5	10×10^3	15×10^3	25×10^3
	9.3				1.17×10^{18}	1100.0	13.5	8.0×10^3	18×10^3	26×10^3
	10.0				6.3×10^{17}	1117.5	20.0	19×10^3	12×10^3	31×10^3
	10.5				7.0×10^{17}	1115.0	17.0	20×10^3	13.5×10^3	33.5×10^3
	11.0				7.6×10^{17}	1115.0	22.0	24×10^3	14.5×10^3	38.5×10^3
3	7.5	5.21	7.10	42.75	1.3×10^{18}	1167.5	22.5	8.0×10^3	18×10^3	26×10^3
	8.5				6.2×10^{17}	1187.5	24.5	19×10^3	12×10^3	31×10^3
	10.0				1.5×10^{18}	1165.0	23.0	19×10^3	18×10^3	37×10^3
	10.5				9.4×10^{17}	1175.0	40.0	24×10^3	15×10^3	39×10^3
	11.0				9.4×10^{17}	1170.0	48.6	26×10^3	16×10^3	42×10^3

ζ=Zeta potential, mv (mel volt)
ϕ_o= Surface potential, mv
n=number of ions per cubic meter
σ= Charge density by esu/cm^2 (electrostatic unit per square meter)
S= Surface area
CEC= Cation Exchange Capacity

TABLE 3 . Charge distribution of some calcareous soils after removal of $CaCO_3$ at different pH values.

Soil No.	pH	S (m^2/g)	CEC meq/100 soil	$CaCO_3$ %	n Ions/cm^3	ϕ_o mv	ζ mv	σ_1 (esu/cm^2)	σ_2 (esu/cm^2)	σ Total (esu/cm^2)
1	8.3	4.95	7.20	23	8.6×10^{18}	1050.0	16.0	62×10^3	25×10^3	87×10^3
	9.3				9.4×10^{18}	1072.5	36.0	66×10^3	24×10^3	90×10^3
	10.0				1.0×10^{19}	1055.0	56.0	67×10^3	26×10^3	93×10^3
	10.5				$1.2 x10^{19}$	1060.5	62.0	69×10^3	28×10^3	97×10^3
	11.0				$1.0 x10^{19}$	1058.0	75.0	71×10^3	26×10^3	97×10^3
2	8.3	5.69	4.60	38	9.4×10^{17}	1107.5	36.0	14.7×10^3	15×10^3	$29.7 x 10^3$
	9.3				1.7×10^{18}	1092.5	28.0	12×10^3	20×10^3	$32 x 10^3$
	10.0				1.1×10^{18}	1100.0	25.0	19×10^3	16×10^3	35×10^3
	10.5				1.4×10^{18}	1097.5	44.0	20.6×10^3	19×10^3	$39.6 x 10^3$
	11.0				$1.4 x10^{18}$	1100.0	48.5	21×10^3	19×10^3	40×10^3
3	7.5	5.21	7.10	22.5	$1.56 x10^{18}$	1165.0	23.5	15×10^3	20×10^3	35×10^3
	8.5				$1.17 x10^{18}$	1170.0	40.0	23×10^3	17×10^3	40×10^3
	10.0				2.6×10^{18}	1150.0	33.0	29×10^3	19×10^3	48×10^3
	10.5				$2.3 x10^{18}$	1155.0	49.0	30×10^3	21×10^3	51×10^3
	11.0				$2.18 x10^{18}$	1156.0	52.0	34×10^3	22×10^3	56×10^3

Soil electrical properties

This work dealed with the contribution of calcium carbonate on the charge density of the calcareous soils. Zeta potential, surface potential and different electrical properties of three calcareous soils before and after removing some of the calcium carbonate are presented in Tables 2 and 3 respectively. Zeta potential as well as surface charge density was determined under different $CaCO_3$ contents and pH values. The results exhibited that as the $CaCO_3$ content decreased the zeta potential increased. This decrease in $CaCO_3$ content reflected on the amount of charges, as the $CaCO_3$ decreased the surface charge density increased.

Effect of calcium carbonate and pH on the electrical properties of some selected calcareous soils

Before discussing the effect of calcium carbonate and pH on the charge density and the electrical surface potential we have to mention that there are two types of surfaces: -

1. Constant potential surfaces (reversible interface) such as oxides, *i.e.*, amphoteric surfaces, the charge changes with changing concentration of the indifferent electrolyte and the surface of such oxides contain ions that are not fully coordinated and hence become electrically charged.
2. Constant charge surfaces (irreversible interface) such as phylosilicates (clay minerals) isomorphous substitution. They have variable surface potential. The charge of the surface is fixed and remains independent of solution composition. The surface electrical potential is sensitive to indifferent electrolyte concentration, (Sposito , 1984).

From results of this study; presented in Tables 2 and 3 it was found the contribution of the reversible interface type surface, increases with two factors *i.e.*, pH and the colloidal $CaCO_3$ fraction. The results indicated that there is a change in the charge density with changing the $CaCO_3$ content and the pH. Where, as the $CaCO_3$ content decreases the surface charge density increases (Fig.2). Contrary to that the surface potential was not sensitive to any change in $CaCO_3$ content as well as pH.

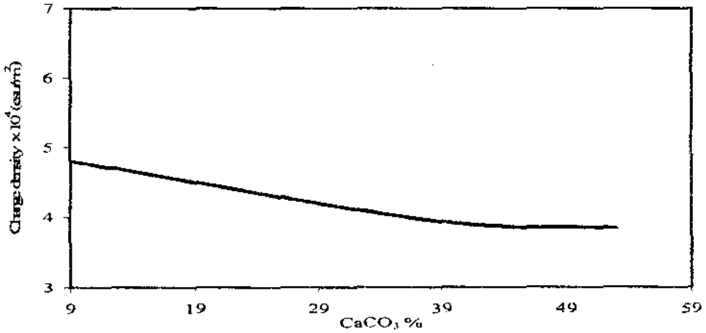

Fig. 2. Effect of calcium carbonate content on the charge density.

This behavior was due to the nature of the surfaces. Under these conditions the surfaces are mainly reversible interface *i.e.,* constant potential surfaces. The increasing of charge density with decreasing $CaCO_3$ content from 33.1% to 23% and from 53% to 38% and from 42.75% to 22.5% for soils 1, 2 and 3 respectively at a certain pH value was attributed to the predominance of clay particles; as $CaCO_3$ content decreased; in the soil suspensions; which in turn increased the contribution of the clay particles; the charge density increased.

Zeta potential was more pronouncing at lower $CaCO_3$ content and this can be attributed to the fact that Ca^{2+} ion with its small hydrated radii (r_h), distance of closest approach (a_o) and high polarizability, approaches the surface more readily and becomes specifically adsorbed and thus its effects on zeta potential was more significant (Faiz & Shams, 1986; Manciu & Ruckenstein, 2003 and Klemen *et.al.,* 2001).

Figure 3, showed the charge density (esu/cm^2) at different $CaCO_3$ contents and pHs. The results revealed that as the pH increased the charge density increased, and this was due to approaching the isoelectric point of $CaCO_3$ (pH, 10) (www.colloidal-dynamics.com, 1999). Before the isoelectric point $CaCO_3$ particles carry positive charges, but as the pH increases nearby the $CaCO_3$ isoelectric point the negative charges on the soil surface increase inducing higher charge density (Sposito, 1984).

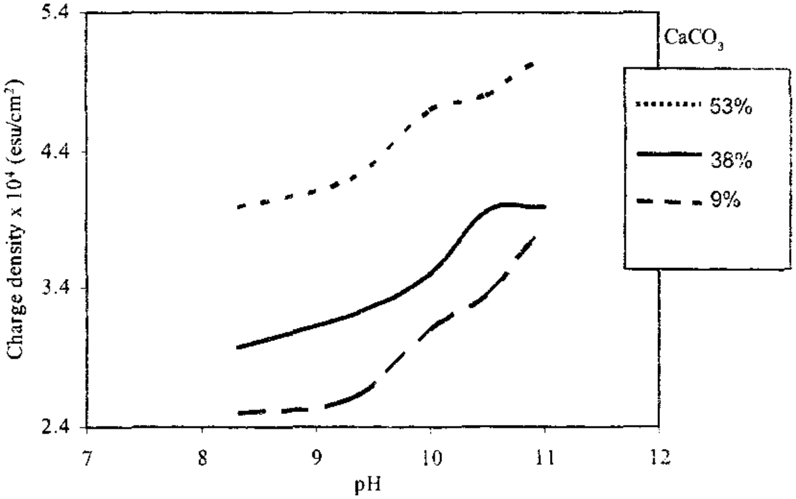

Fig. 3. Charge density at different pH values with different calcium carbonate percent .

Distribution of charges in the double layer

The total surface charge density of the double layer ($\sigma = \sigma_1 + \sigma_2$) represents two parts. The first one (σ_1, Stern or specific adsorption layer) is close to the surface and the specific adsorption of ions is considered on this part. The second (σ_2, Gouy or nonspecific adsorption layer) is representing the nonspecific ion adsorption.

The total charge density was calculated through surface area and cation exchange capacity as presented in equation (3). The Gouy layer charges (σ_2) were calculated from equation (4) while (σ_1) was obtained by the difference between equations (3 and 4). The general trend of the charge density was that (σ_1) was higher than (σ_2) as $CaCO_3$ content decreased; according to the high contribution of clay minerals the specific adsorption, which located at this part increased.

Conclusion

The distribution of charge in the electrical double layer of the clay fraction of these calcareous soils was changed due to changing in $CaCO_3$ content and pH. For instance σ_1 values of the three soils after removal of $CaCO_3$ at different pHs were much higher than its values before removing of $CaCO_3$ at the same pHs. The type of the clay minerals identified using x-ray diffraction can help us for more accurate estimation of the amount and distribution of mobile, σ_2, and restricted, σ_1, affecting adsorbed ions on calcareous soils.

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تأثير كربونات الكالسيوم على توزيع الشحنات الكهربية على أسطح الأراضى الجيرية

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أربعة معادن طين هى مجمل ما تم تحديده فى الجزء الطينى الذى فصل من ثلاثة عينات من التربة الجيرية وقد استخدمت أشعة إكس لتحديد هذه المعادن . الحركية الكهربية (V_{el}) لحبيبات الجزء الغروى تم قياسها عند أرقام مختلفة من الحموضة ومحتويات متغيرة من كربونات الكالسيوم . كذلك حسب الجهد الزيتى (ζ) بدلالة الحركية الكهربية . حسبت كثافة الشحنة بدلالة السعة التبادلية الكاتيونية و مساحة السطح للجزء الطينى المستخدم وكان توزيع الشحنات فى الطبقة الكهربية المزدوجة للجزء المستخدم متغيرا تبعا لمحتوى كربونات الكالسيوم فى الوسط و رقم الحموضة . أما الجهد الزيتى فكان واضحا عند المحتوى المنخفض من كربونات الكالسيوم . وكانت الشحنات المسئولة عن الإدمصاص النوعى (σ_1) للتربة المستخدمة أعلى من الشحنات المسئولة عن الإدمصاص غير النوعى (σ_2) عند المحتوى المنخفض من كربونات الكالسيوم مما يدل على زيادة كثافة الشحنة بإنخفاض محتوى التربة من كربونات الكالسيوم .