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SURFACE CHARGE EVALUATION OF SOILS,

CLAYS AND OXIDES.

by

Martin Duquette °

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

· ·

Department of Renewable Resources McGill University, Montreal.

September, 1991 °



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Suggested Short Title

SURFACE CHARGE EVALUATION

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ABSTRACT

Two objectives are achieved in this thesis: (1) to develop a new method to measure the pH-dependent net surface charge of soils and (2) to determine if, by a combination of the surface charge evaluated by potentiometric titration and ion adsorption, we can separate the permanent charge, generated by the isomorphous substitution, from the variable charge. First, a laboratory procedure, using backtitration, was developed for the measurement of the pH-dependent net surface charge. This method was tested on ten soil horizons from Gleysols and Podzols. It appears that the pH-dependent net surface charge, measured by this technique, shows good agreement with that measured by ion adsorption. It is also possible, with this method, to identify some plateaus and inflection points in the backtitration curve associated with protonation/deprotonation reactions of specific soil components. Secondly, it was demonstrated that it is possible to increase the surface charge of montmorillonite with Aloxide coatings under specific conditions.

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RÉSUMÉ

Deux objectifs sont atteints dans ce travail; (1) le dévelopement d'une nouvelle méthode permettant la détermination des charges de surface dépendantes du pH pour les sols, et (2) en utilisant les titrages potentiométriques et les mesures d'adsorption d'ions, vérifier si l'on peut séparer les charges permanentes des charges variables dans un mélange chimique d'une argile et d'un oxide d'aluminium. Dans un premier temps, une méthode de laboratoire, utilisant des titrages est élaborée afin de mesurer les charges nettes dépendantes du pH. Cette méthode est testée sur dix horizons de sols provenant de gleysols et de podzols. Les résultats de cette méthode, pour la détermination des charges de surface, montrent une très forte similarité avec ceux déterminés par Il est aussi possible, utilisant cette adsorption d'ions. méthode, de distinguer une série de plateaux et de point d'inflections dans les courbes de titrages, correspondant à des reactions de protonations/déprotonations de surface de certaines composantes du sol. Dans un deuxième temps, il est démontré qu'il est possible d'augmenter la charge de surface d'une montmorillonite lorsque celle-ci est enrobée avec des oxides d'Al.

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LIST OF ABREVIATIONS AND SYMBOLS

Sec. 1

| a | Correction factor for unit |
|---|--------------------------------------|
| | conversion. |
| A | Anion species. |
| AEC | Anion exchange capacity. |
| Alm | Monomeric aluminum. |
| ≡Aloh | Aluminol surface group. |
| Alp | Polymeric aluminum. |
| b | Linear slope of the absorption |
| | curve. |
| с | Cation species. |
| CEC | Cation exchange capacity. |
| d (000) | Plane of diffraction. |
| a _c | specific density of clay. |
| dQv/dpH | Slope of the variable surface charge |
| | as a function of pH. |
| EM | Electrophoretic mobility. |
| F | Faraday constant. |
| HAI | Hydroxy aluminum interlayer. |
| IEP | Isoelectric point. |
| IEPS | Isoelectric point of the solid. |
| IR | Infrared. |
| к, к _i , к _j | Absorbance indexes. |
| K _{a1} ^s , K _{a2} ^s | Surface protonation constant. |

| K _{a1} ^s (int), K _{a2} ^s (int) | Intrinsic surface protonation |
|--|---|
| | constant. |
| K _(i) | Equilibrium constant for the |
| | variable surface charge of a site |
| | njn. |
| К _{so} | Solubility constant. |
| М | Molar concentration. |
| N _{base} | Normality of the base used to |
| | backtitrate. |
| N, | Normality of species i. |
| n _i | Number of plates per tactoid of Ca- |
| | montmorillonite. |
| n _j | Number of plates per tactoid of Li- |
| | montmorillonite. |
| n_1 to n_5 | Mole number of the i th chemical |
| | species in a reaction. |
| OD | Optical density. |
| PDI | Potential determining ion. |
| pH _{pznpc} | Point of zero net proton charge. |
| PPZC | Pristine point of zero charge. |
| ₽₩ | Negative log of the self-ionization |
| | constant of water. |
| PZNC | Point of zero net charge. |
| PZSE | Point of zero salt effect. |
| Q* | H ⁺ /OH ⁻ consumption during titration, |
| | without dissolution of the solid |

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phase.

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| Q | H ⁺ /OH ⁻ consumption during titration, |
|---|---|
| | with dissolution of the solid phase. |
| Qm _(i) | Total surface charge of the site |
| | number "i". |
| Q _{net} | Total surface charge. |
| Qoct | Charge reduction in the octahedral |
| | layer. |
| Qp | Correction factor to adjust the pH- |
| | dependent CEC to a known value of |
| | the CEC at a given pH. |
| Qtet | Charge reduction in the tetrahedral |
| | layer. |
| Qtot | Total charge reduction. |
| Qv | Variable charge. |
| QV _(i) | Variable surface charge of site "i". |
| R | Gas constant. |
| Ri | Shannon-Prewitt radius. |
| R ² | Correlation coefficient. |
| ≡SiOH | Silanol surface group. |
| ≡S _(i) OH, ≡S _(i) O | Surface functional group of the site |
| | number "i". |
| =SOH ₂ ⁺ , =SOH, =SO ⁻ | Surface functional group. |
| SSA | Specific surface area. |
| SV | Sedimentation volume. |
| т | Absolute temperature. |
| | |

| TEM | Transmission electron microscope. |
|---------------------|--------------------------------------|
| v _o | Initial volume of the suspension |
| | before backtitrating. |
| V _{sample} | Volume of base added during the |
| | sample titration. |
| V _{SN} | Volume of the supernatant titrated. |
| Vreference | Volume of base added during the |
| | reference titration. |
| W _{soil} | Weight of the soil. |
| x | Layer charge. |
| XAl | Fraction of Al dissolved from the |
| | tetrahedral layer. |
| XMg | Fraction of Mg dissolved from the |
| | octahedral layer. |
| z, z _i | Valence. |
| z_ | Valence of anion. |
| z, | Valence of cation. |
| ZPC | Zero point of charge. |
| ZPT | Zero point of titration. |
| ∆g _r ° | Standard Gibbs energy change. |
| ΔG _r *] | Standard Gibbs energy change, |
| | corrected for an adsorbed ion and |
| | the layer charge. |
| ß | Major particle dimension. |
| Г | Surface charge resulting from a |
| | titration of a non-dissolving solid. |
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Surface charge resulting from a Γ* titration of a dissolving solid. OH consumed in the sample titration. $\Gamma_{\rm sample}$ Surface charge due to pH-dependent Γ_{surface} surface functional group. consumed in the reference $\Gamma_{\rm reference}$ OH titration. Activity coefficient. Υī Wavelength. λ Chemical standard potential. μ• Summation. Σ Ψ Surface potential. Ion concentration. []

PREFACE

This thesis is focussed on surface charge determinations. Chapter I is an introduction to the topic containing historical development and specific research objectives. Chapters II and III are the theoretical development and the applications of a backtitration technique for surface charge measurement of soils. Because the three first chapters are closely related no connecting paragraphs between them are presented. Chapter IV is devoted to the effect of the Al oxide coatings on the surface charge behavior of а montmorillonite clay sample. It is to be noted that a minor part of the data for the ion adsorption method and soil properties used in the chapter III has been taken from two earlier published papers, co-authored by the advisor of the candidate, Dr. W.H. Hendershot (Duquette, M. and W.H. Hendershot, 1987. Contribution of exchangeable aluminum to cation exchange capacity at low pH. Can. J. Soil Sci., 67:175-185 and Hendershot, W.H. and M. Duquette, 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. Soil Sci. Soc. Am. J., 50:605-608).

Research included in this thesis, from the conception of idea to the realisation of this thesis, is the work of the candidate. The role of Dr. Hendershot was that of supervision

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and contributed through discussion of the candidate's ideas and editorial assistance in the preparation of the thesis.

In keeping with the "Guidelines Concerning Thesis Preparation" the following paragraph is reproduced in full:

" The inclusion of manuscripts co-authored by the candidate and others is acceptable but the candidate is required to make an explicit statement on who contributed to such work and to what extent, and supervisors must attest to the accuracy of the claims, e.g. before the Oral Committee. Since the task of the Examiners is made more difficult in these cases, it is in the candidate's interest to make the responsabilities of authors perfectly Candidates following this option must clear. inform the Department before it submits the thesis for review."

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I would like also to thank a friend of mine, for providing the infra-red spectra of the minerals. Financial support for this work was provided partially by a scholarship from the FCAR and through research grants from NSERC and FCAR.

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CONTRIBUTION TO KNOWLEDGE

Surface charge measurement in soils, by potentiometric titrations, has been at the center of a controversy. Because dissolution of the solid phase occurs, proton consumption is difficult to attribute to surface reactions (adsorption) alone and thus the pH-dependent surface charge usually does not correspond to that measured by ion adsorption. However, we have found that a backtitration technique, with a proper reference backtitration can eliminate these problems.

The following thesis contains two major contributions to scientific knowledge in soil science. In the first three chapters a backtitration technique is developed to measure the pH-dependent net surface charge of soils. The pH-dependent surface charge measured by this technique shows good agreement with the surface charge measured by ion adsorption. Moreover, the resulting titration curves for surface charge development can be modeled with a minimum knowledge of the chemical constituents of the soils. This backtitration technique is appropriate for surface charge measurement, because: (1) it reproduces the results obtained by the ion adsorption method and (2) it is less time consuming.

In chapter IV, the surface charge of a montmorillonite with different proportions of the CEC blocked by Al-oxide precipitated onto the surface is measured. From this

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experiment, three conclusions can be drawn: (1) the backtitration method developed in chapter II and III functioned well with montmorillonite, Al-oxide and chemical mixtures of both, (2) in contrast to what is usually found in the literature, the surface charge of Al-oxide coating on montmorillonite increases the CEC only when base or acid are added to the suspension, and (3) it is shown that it is not possible to evaluate the permanent charge of a chemical mixture of montmorillonite and Al-oxide, using the model of Uehara and Gillman (1980).

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CHAPTER I

GENERAL INTRODUCTION

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1.0 General Introduction

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1.1 Origin of Surface Charge in Soils

In soils, the minerals controlling most of the surface charge are found in the clay-size fraction; because of their high surface area, the clay colloids are the most reactive size fraction. The colloids in soils can be divided into three main groups, inorganic, organic and living colloids. The inorganic colloids include all silicate and aluminosilicate minerals and oxides, hydroxides, oxyhydroxides, carbonates and sulphates. Through their surface functional groups they are able to adsorb and complex ions in the immediate environment. Two kinds of inorganic surface functional groups are recognized on oxides and silicates; the siloxane ditrigonal cavity and the hydroxyl group.

In the aluminosilicate minerals, specifically the phyllosilicates, the surface charge is controlled by isomorphous substitution either in the tetrahedral sheet $(Al^{3+}$ for Si⁴⁺) or in the octahedral sheet $(Fe^{2+}, Mg^{2+} \text{ for } Al^{3+})$. This isomorphous substitution leaves a charge deficit at the siloxane surface of the tetrahedral sheet that must be balanced by the adsorption of cations. The charge deficit caused by this isomorphous substitution is often referred to by the term "permanent charge", meaning that this amount of charge will be constant whatever the pH of the system. At the

edges of these minerals broken tetrahedral and octahedral sheets are mainly made up of silanol (=SiOH) and aluminol (=AlOH) groups that became charged upon adsorption of potential determining ions (PDI: H⁺ or OH⁻). Consequently, the charge generated by protonation reactions at the edges is referred to by the term "pH-dependent or variable charge". It is recognized that the aluminol groups can complex protons (H⁺) and hydroxyls (OH⁻) and form inner-sphere complexes with oxyanions such as PO_4^{3-} . On the other hand, the silanol groups, due to the high charge of silica, can complex only hydroxyls, and cannot form inner-sphere complexes with oxyanions. However, metal cations can form inner-sphere complexes with both aluminol and silanol groups.

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In the oxides, hydroxides and oxyhydroxides of Fe, Al, Si and Mn, the surface charge is controlled almost exclusively by the adsorption of potential determining ions such as H^{*} and OH^{*}. These minerals are usually amphoteric in nature, being positively charged at low pH (\equiv SOH₂^{*}), neutral at the pH equal to the zero point of charge (\equiv SOH), and negatively charged at high pH (\equiv SO⁻); where \equiv S stands for a metallic cation forming the crystal. At equilibrium, the charge at the surface will be controlled by the solution pH and the concentration of electrolyte. These colloids are characterized by the second type of surface functional group (hydroxyl group). This consists of OH ions bound to the solid phase and forming the surface of the mineral. The reactivity of this group for

complexation reactions will depend on whether the OH is bound to one, two or three metallic cations forming the crystal.

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> The organic colloids in soils, called humic substances, originate from the partial or total decomposition of organic residues. The charge at the surface of the humic substances is controlled by the different surface functional groups such as carboxyl (-COOH), carbonyl (-CO), amino (-NH₂), imidazole (Ring-NH), phenylhydroxyl (Ring-OH), sulfhydryl (-SH) and sulfonic (-SO₂OH) (Sposito, 1984). The complexity and the range of stability for proton complexation (weak to very strong) of these functional groups is so variable that the charge characteristics of the surface of the humic substances are still not well understood.

> The third group of soil colloids are the "living colloids". They are probably the group the least studied with respect to surface charge chemistry. This group includes viruses and bacteria possessing surface functional groups that may be either charged or uncharged.

1.2 Determination of Surface Charge

1.2.1 Potentiometric Titration Methods

One of the commonly used techniques of measuring surface charge is potentiometric titration. This technique has been applied to soils since the beginning of this century. Veith

(1904) employed potentiometric titration to measure soil acidity. Bradfield (1923, 1924) in his study of the nature of soil acidity showed that it was possible to obtain inflection points by adding a strong base to a soil.

Low (1955) showed that it was possible, to attribute the inflection point and the end point of the titration to the amount of exchangeable Al and total acidity in a bentonite suspension. Later Mitra et al. (1963) pointed out that three inflection points could be detected in base titration of montmorillonite suspensions. These inflection points corresponded to the strong H^* , exchangeable Al and weak acid component of the clay, but no surface functional groups were defined in term of reactivity.

Parks and de Bruyn (1962) used potentiometric titrations on crystalline ferric oxide (Fe_2O_3) to assess the adsorption isotherms of H⁺ and OH⁻. Assuming only one type of OH group, capable of reversing its charge on pH variation, they concluded that there is a similarity between the surface reaction:

> $Fe(OH)_2^+$ (surface) \Rightarrow FeO_2^- (surface) + 2H⁺ [1.1] pK (surface) = 8.5 = ZPC

and the solution reaction:

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$$Fe(OH)_{2}^{+} + 2H_{2}O \Rightarrow Fe(OH)_{4}^{-} + 2H^{+}$$
 [1.2]

pK (solution) = 8.5 = IEP of hydroxo-complexes stating that both pK's would be approximately equal; the zero point of charge (ZPC) of the surface is equal to the

isoelectric point (IEP) of the solution of metal hydroxocomplexes. However, the ZPC's of such oxides have been found to be dependent on the properties of the metallic cations, their coordination number, the purity of the crystal and the hydration state of the oxide (Parks, 1965).

The paper by van Raij and Peech (1972) was the first application of potentiometric titration to soil particles to model surface charge using the Gouy-Chapman and Stern theory. Potentiometric titration could be used to study an oxide surface because it possesses a completely polarizable surface. Consequently, the use of tropical soils, rich in oxides, to test this method was justified. These authors reported the similarity between the surface charge and the surface potential of the soils compared to those of the oxides. This was one of the first times that a surface charge model was applied to the results of potentiometric titration of soils.

Irregularities appeared in the use of potentiometric titrations to evaluate surface charge of soils. Espinoza et al. (1975) found that the surface charge, as measured by potentiometric titration, was different from that measured by ion adsorption. They explained the difference in their results by the affinity of the potential determining ions for the different surfaces.

Gallez et al. (1976) pointed out that the surface charge evaluated by potentiometric titration shows a ZPC around pH 3.5 to 5.5 for Nigerian soils, emphasizing the relationship

between the surface charge chemistry and the degree of weathering of these soils. With increasing time and weathering, the soil will pass from a dominance of permanent charge to a dominance of pH-dependent charge. This is explained by the fact that more coatings will be formed and therefore more pH-dependent surface charge will be detected by potentiometric titration for older soils than younger ones.

Laverdière and Weaver (1977) stated that reasonable fits of the surface charge as determined by potentiometric titration and ion adsorption could be obtained. However, they found that when permanent charge due to isomorphous substitution is involved in the solid (or mixture), it tends to decrease the ZPC, and increase the displacement of the ZPC from the zero point of titration (ZPT). Hendershot and Lavkulich (1978) and Hendershot et al. (1979) showed that for temperate soils with low amounts of crystalline oxides, the ZPC tends towards the soil pH with increasing pedogenic development.

Pyman et al. (1979) showed that when the solution contains a small amount of anions, capable of being specifically adsorbed, there will be a shift in the cross over point of the titration curves used to determine the ZPC. A recent study shows that even ions such NO_3 and K⁺ can be specifically adsorbed on rutile (TiO₂) and hematite (α -Fe₂O₃) (Gibb and Koopal, 1990). Pyman et al. (1979) defined three ZPC's: (1) the zero point of charge (ZPC), the pH at which the

summation of the charge from all sources equals zero, (2) the isoelectric point of the solid (IEPS): the pH at which the adsorption of potential determining ions (PDI: H^* , OH^-) is zero (Parks, 1967), and (3) the pristine point of zero charge (PPZC) when the ZPC equal the IEPS.

It was also apparent that the surface charge determined by potentiometric titration was a function of the ions adsorbed on the exchange sites, the nature of the electrolyte solution, and whether it contained ions that were adsorbed specifically or non-specifically (Pyman et al., 1979; Stoop, 1980). Depending on the measurement technique used, single samples can give different results for the surface charge. Today potentiometric titration is used to measure the pHdependent surface charge generated by the different soil colloids.

The data provided by this technique are the basis for the surface complexation models used to predict the adsorption of ions onto the surface. In fact, it is always a protonation/deprotonation reaction occurring on a site, defined as \equiv SOH, that is responsible for the surface charge (Morel et al., 1981). The difference in the surface complexation models is only in the definition of the diffuse layer and in the number of planes of adsorption used to model the variation of the surface potential and the surface charge density (Westall and Hohl, 1980).

It is believed by some soil scientists that potentiometric titration measures only the pH-dependent surface charge of soil (Uehara and Gillman, 1980). The pHdependent surface charge determined by this technique has often been used to assess pedogenic development in soils and the agronomic effect of liming (Hendershot and Lavkulich, 1978; Gillman and Sumpter, 1986; Hunter and Busacca, 1987; Gillman and Sumner, 1987).

Schulthess and Sparks (1986, 1987, 1988) proposed a backtitration technique for measuring the surface charge of oxide particles. They argued that the usual methods are not satisfactory because they give a maximum surface charge density that is unlikely to occur on the oxides and also that potentiometric titration does not take into account the solubility of the solid phase during titration. In their papers, the data generated by their backtitration when plotted against pH shows different plateaus and inflection points representing different ion-surface complexation reactions.

1.2.2 Ion Adsorption Methods

Jenny (1932) reported an experiment on soil leaching with KCl salt performed by Gazzari and Way in 1850. These two scientists observed that when the soil column was leached with KCl, the Cl⁻ was eluted with Ca^{2+} , and K⁺ was retained by the soil. This was the first time that the idea of ion exchange

was reported. Adsorption isotherms appear in the literature as early as 1888 with the paper of van Bremmelen, and redefined as the Freundlich adsorption isotherm by Freundlich (Sposito, 1980). At the beginning of the 20th century, Ganssen (1913) reported that the mass action coefficient could be used to characterize binary exchange on aluminosilicates. The mass action coefficient was then expressed either in millimolar concentration or equivalent per mass of exchanger respectively for the ions in solution and on the exchanger. Kerr (1928) suggested that the mass action coefficient was directly related to the soil exchange complex. He considered the soil as being a solid solution rather than a mixture of separated solid phases. The thermodynamic definition of the exchange constant made its first appearance in the literature with the paper of Vanselow (1932); he used ion activity instead of ion concentration.

From the idea that ions could be exchanged at the surface of soil particles, pH-dependent ion adsorption methods were developed to measure total CEC. At the beginning of the method development, the exchangeable cations were removed by electrodialysis or HCl saturation to convert the clay to H^{*} form, and then removing this H^{*} by saturating the clay with a salt solution and titrating the acidity in solution (Gieseking, 1939; Conrey and Green, 1932).

Schofield (1949) provided an ion adsorption method measuring not only the cation exchange capacity but also the

anion exchange capacity. This paper was one of the turning points in the surface charge methodology. His major contribution was to develop an ion adsorption method for measuring net surface charge, and to separate AEC and CEC. This method consists of three steps: (1) the saturation of the exchange sites with a salt solution, (2) the removal of the excess salt by alcohol washing and (3) the replacement of the adsorbed ions by a second salt.

Melich (1953) proposed a method to separate cation and anion exchange capacity. In addition the work of Melich and that of Schofield (1939, 1949), Coleman et al. (1959), Fieldes and Schofield (1960) and Melich (1960) proposed several methods involving a combination of titration (soil acidity) and ion exchange to differentiate between the permanent and the pH-dependent CEC. Ion adsorption methods were considered to measure the total exchange capacity of the soil.

Pratt and Holowaychuk (1954) found differences in the CEC measured on soils by $NH_4(C_2H_3O_2)$, $Ba(C_2H_3O_2)_2$ and buffered $BaCl_2$ salt. Referring to the $BaCl_2$ method as being the most precise, they separate the pH-dependent CEC from the total CEC by observing that the titratable acidity was almost equal to the difference in the CEC between pH 8 and 3 (Pratt, 1961).

Modifying the method of Schofield (1949) by elimination of the alcohol washing step and determining the amount of entrained salt solution by weighing, Wada and Harada (1969) avoided the problem of hydrolysis and the re-expansion of the
double layer at very low electrolyte concentration (Wada and Harada, 1969; Sumner, 1963). However, the final results of the CEC determination were different according to the salts used, at least for some clay minerals (Wada and Harada, 1969). This problem had been pointed out by Sumner (1963). Bascomb (1964) used a Ba-saturated soil without an alcohol washing step and a replacing solution of $Mg(SO_4)$; titration of the Mg remaining in solution allowed the calculation of CEC.

Sumner and Davidtz (1965) observed that the CEC, AEC and charge of a soil must be determine at the field pH. net Because of the pH-dependent surface charge of the soil, the use of a buffered method at high pH (8.2) can qive unrepresentative results. Using multiple regression analysis on CEC determination of soils, calculated by the summation of the exchangeable cation, Wilding and Rutledge (1966), McLean and Owen (1969) and Hallsworth and Wilkinson (1958) showed that it was possible to differentiate the contribution of clay and organic matter to the total CEC. This observation is important because it implies that the total surface charge of soils is generated by more than one soil constituent. Thus the total CEC can be measured and it is possible to differentiate between the contribution of the organic matter and the clay to the total CEC. Curtin and Smillie (1976) prefered to use organic matter and the specific surface area instead of the clay content to explain the CEC.

Juo et al. (1976) tested three methods of CEC; they concluded that different results are obtained for the CEC depending of the method used; for routine soil analysis, the CEC must be measured at the soil pH. Morais et al. (1976) observed that different salts used for AEC and CEC determination gave different results, emphasizing the fact that the nature and the valence of the counter ions of the electrolyte solution have a direct effect on the surface charge properties of soils. Wada and Okamura (1980) showed that electrolyte concentration affects the surface charge, and that soils containing amorphous coatings of Al, Fe and organic matter exhibit the highest pH-dependent CEC. Edmeades and Clinton (1981) proposed a SrCl, method for determining CEC. Their method is fast and avoids the use of suppressing agent Ca²⁺ and Mg²⁺ needed to prevent Al interference on determination by atomic absorption spectrometry.

In addition to the problems caused by hydrolysis and the salt effect on the surface charge determined by ion adsorption methods, the problem of exchangeable Al became apparent. Bache (1970) reported the possibility that the charge of adsorbed Al was less than three, suggesting that some polymeric form of Al $(Al_x(OH)_y^{(3x-y)*}; where x > 1)$ was also adsorbed. Espinoza et al. (1975) pointed out that NO_3^- adsorption and the potentiometric titration did not give the same value for AEC. They explained this discrepancy by the fact that upon acid addition Al was released from the solid

phase. This point has also been suggested by Kinjo and Pratt (1971a, 1971b). Bolland et al. (1976) showed that the pHdependent surface charge of kaolinite was not due to the protonation reaction but to the strongly adsorbed Al on the exchange sites. This Al was not taken into account in most CEC methods, consequently an over estimation of the pHdependent CEC ($CEC_{pH8}-CEC_{pH3}$) was observed. Duquette and Hendershot (1987) showed that even if exchangeable Al is taken into account, it does not balance all of the pH-dependent CEC for soils in Quebec.

1.3 Permanent Versus pH-dependent Surface Charge

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The distinction between the permanent and the pHdependent charge has caused confusion among the soil scientists. As reported by Melich (1981), in 1979 a subcommittee of the Soil Science Society of America (SSSA) on soil chemistry terminology redefined permanent charge as:

> "the net negative (or positive) charge of clay particles inherent in the crystal lattice of the particle ; not affected by changes in pH or by ion exchange reactions."

This definition corresponds to the charge associated with the isomorphous substitution inside the crystal. In soils, this definition can lead to some confusion because the sum of the individual permanent charge of all clay minerals constituting the soil is not necessarily the permanent charge

of the soil. In fact, the soil particles are coated with amorphous inorganic and organic materials and a blockage of some permanent charge sites occurs (Sumner, 1963; Davidtz and Sumner, 1965; Oades, 1984; Keren, 1986). However, it has been reported that the addition of Al-polymers to montmorillonite and the removal of amorphous and oxide coatings in soils can increase or decrease the CEC and the power of the soil to adsorb heavy metals (DeKimpe et Laverdière, 1980; Keren, 1980; Elliott et al., 1986). The question here is in what cases will the permanent charge of the clay particles correspond to the permanent charge of a soil?

The methods of Fey and Leroux (1976) or van Raij and Peech (1972) are the most commonly used ion adsorption and potentiometric methods for measuring total CEC, AEC and pHdependent charge. Gillman and Uehara (1980) and Uehara and Gillman (1980) proposed a method in which the results of potentiometric titration and ion adsorption methods can be used to calculate the permanent and the pH-dependent charges. They assumed that potentiometric titration will measure only the variable charge component of the soil. At the cross over point of titration curves in different electroJvte concentration (PZSE) the net surface charge of the coatings is zero. By measuring the CEC by ion adsorption at this pH (pH=PZSE) they assumed that they obtained the permanent charge of the mixture. However, some soil scientists think that potentiometric titration measures the charge on all the soil

particles (Hendershot and Lavkulich, 1983). The confusion comes from the fact that in some cases potentiometric titration of H^+ - or Al-saturated soils will give the same results for the CEC as the conventional ion adsorption methods (Laverdière and Weaver, 1977).

The model of Gillman and Uehara (1980) has been severely criticized. For their model to be valid, it must take into account the effect of the permanent charge on the surface potential calculated by the Nernst equation (Madrid et al., 1984). It has been demonstrated that a small amount of permanent charge in a given suspension can affect the surface chemistry of the oxide component (Kleijn and Oster, 1983). Also when the PZNC varies with the electrolyte concentration this is taken as evidence of the presence of permanent charge; this situation occurs even if no permanent charge exists (Wada and Okamura, 1983). The link between the charge measured by potentiometric titration method and ion adsorption is still unclear.

1.4 Surface Reactions

This part deals only with the different ways in which surface reactions lead to the creation of surface charge on an amphoteric solid. The equations presented in Table 1.1 are the basic equations that described pH-dependent surface charge reactions.

| Surface Reaction Equations | |
|--|--|
| Surface protonation reactions | $K_{a1}^{3}; \equiv SOH_{2}^{*} \Leftrightarrow \equiv SOH + H^{*}$ |
| | K_{a2}^s ; =SOH \leftrightarrow =SO ⁻ + H ⁺ |
| Intrinsic equilibrium constants | $K_{al(intrinsic)}^{s} = \frac{[=SOH] [H^{*}]}{[=SOH_{2}^{*}]} \exp\left(\frac{-F\Psi}{RT}\right)$ |
| | $K_{a2(intrinsic)}^{S} = \frac{[=SO^{-}] [H^{*}]}{[=SOH]} \exp\left(\frac{-F\Psi}{RT}\right)$ |
| Assumptions | $\frac{\gamma_{H^*} \gamma_{=SOH}}{\gamma_{=SOH_2^*}} = \frac{\gamma_{=SO^*} \gamma_{H^*}}{\gamma_{=SOH}} = \exp\left(\frac{-F\psi}{RT}\right)$ |
| | [=SOH] _T = [=SOH ₂ ⁺] + [=SOH] at pH < ZPC [=SOH] _T = [=SO ⁻] + [=SOH] at pH > ZPC |
| Net surface charge | $Q_{NET} = [\equiv SOH_2^*] - [\equiv SO^-]$ |
| <pre>F: Faraday constant. T: Absolute temperature. y: Activity coefficient. [=SOH₂*], [=SOH], [=SO]: Con group.</pre> | T: Surface potential. R: Gas constant. [≡SOH] _T : Total concentration of surface group. centration of positive, neutral and negative surface functional |

Table 1.1 Surface reaction equations.

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The solution of the equations in Table 1.1 is usually done by the analysis [^] potentiometric titration data for a suspension. The following assumptions are usually made when considering these equations; (1) the H⁺ and OH⁻ added react only with the surface through protonation reactions and (2) no dissolution of the solid occurs during the titration. Consequently the charge balance due to H⁺ and OH⁻ is regulated by the pH of the solution and the surface charge.

In a pure oxide system, these assumptions are generally In soils, dissolution takes place. confirmed. Because of this, during potentiometric titration OH and H ions will react with the solid phase releasing hydrolysable ions such Al³⁺ and Fe³⁺ into solution. However, there are some soils for which these assumptions are respected. This is the case for the potentiometric titration of Oxisols, in which the minerals dominating the solid phase are well crystallized oxides and kaolinite that do not dissolve easily (Charlet and Sposito, 1987). Also, the potentiometric titration technique worked well with river sediments that were previously acid washed for several hours, minimizing the risk of dissolution during the titration; surface complexation models were then applied to the data obtained (Mouvet and Bourg, 1983). The different surface complexation models are based mainly on the definition of the electric double layer involving only one type of amphoteric functional group (Westall and Hohl, 1980). These models included: (1) the constant capacitance model (Goldberg

and Sposito, 1984a, 1984b; Goldberg, 1985), (2) the diffuse layer model (Huang and Stumm, 1973), (3) the Stern model, (4) the triple layer model (Davis et al., 1978; Davis and Leckie, 1978, 1980) and (5) the Stern model adapted by Bowden et al. (1977).

In soils it seems that more than one constituent can control the surface charge, i.e. humic and fulvic acid, amorphous coatings, clay minerals, etc. Because of the relative solubility of some of these constituents in soils from temperate areas, it is more realistic to model the surface charge using a multisite adsorption model. Similarly, a titration technique must be developed to account for the effect of hydrolysable ions in solution. Currently, some models exist for multisite adsorption involving different reactivities of the surface functional groups on hydrous oxides, depending on whether the oxo (=SO) or hydroxo (=SOH) surface functional groups are coordinated to one, two or three metal cations inside the crystal structure (Hiemstra et al., 1989a, 1989b; Gibb and Koopal, 1990). This implies that for a single oxide the different planes at the surface of the crystal will have different affinities for OH and H* adsorption. With the exception of this new model (Hiemstra et al., 1989a, 1989b), multisite adsorption is usually solved for a mechanical mixture of two minerals (Madrid et al., 1984; Madrid and Diaz-Barrientos, 1988; Kuo and Yen, 1988).

1.5 Specific Research Objectives

Following the discussion in this chapter, it is evident that problems exist in the determination of the pH-dependent surface charge of soils. The problems originate from (1) H^+/OH^- consumption during potentiometric titration when the solid phase titrated has a tendency to dissolve and (2) the inequality often observed for the pH-dependent charge determined by ion adsorption and potentiometric titration methods. In addition, ion adsorption methods are time consuming and not appropriate for routine laboratory analysis. In addition to the problems mentioned above, we believe that the approach of Gillman and Uehara (1980) and Uehara and Gillman (1980), who proposed a means of separating permanent from variable charge, is not correct. Consequently, the specific research objectives of this study are:

- (1) To develop an analytical method that will permit good agreement of the pH-dependent surface charge measured by ion adsorption.
- (2) To construct a surface charge model that will differentiate among the charges generated by different soil constituents.
- (3) To determine if, by a combination of the surface charge evaluated by potentiometric titration and ion adsorption, we can separate the permanent charge, generated by the isomorphous substitution, from the variable charge.

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CHAPTER II

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## EVALUATION OF THE SURFACE CHARGE OF CLAYS, SOILS AND OXIDES.

## I. THEORY.

2.0 Evaluation of Surface Charge of Clays, Soils and Oxides.I. Theory.

#### 2.1 Introduction

In the literature, different models are used to calculate the pH-dependent surface charge of a particular solid (Westall and Hohl, 1980). The models use as input the results of potentiometric titration or ion adsorption measurements. Development of a surface charge model is done in two steps. First, a laboratory method must be developed to measure the properties needed for the model. The method used must be precise, not only for the accuracy of the results, but also for a clear identification of what exactly has been measured. The second part in modelling is to develop a mathematical model that will reproduce results obtained and provide a satisfactory explanation of the results both on a chemical (or molecular) and mathematical basis.

Most models of surface charge chemistry of soils have been derived quantitatively from data obtained through potentiometric titration (Sposito, 1984). Such models are usually described under the general term of surface complexation models and all require electroneutrality, charge and mass balance equations and speciation of ions in solution (Morel et al., 1981; James and Parks, 1982). Once the data have been analyzed, the experimenter, depending on the model,

is able to derive either the capacitance term in the double layer or the intrinsic equilibrium constants specific for the adsorption or the complexation reaction at the solid/solution interface (Westall and Hohl, 1980). However, models that are based on oxide systems often give unsatisfactory results when applied to soil surface charge chemistry. If the soil used contains solid phases that are similar to the solid phases for which a particular model was developed, then there is a good chance that the model will be successful. This is usually the case of models such as the constant capacitance model (Goldberg and Sposito, 1984a, 1984b; Goldberg, 1985), the triple layer model (Koopal et al, 1987) or the four layer model (Bowden et al., 1980) that are used to describe the adsorption and surface charge characteristics of soils rich in Al oxides, Fe oxides and kaolinite (Oxisols).

The surface charge behaviour of Oxisols is closely related to those of the oxides (Fe and Al). They possess dominantly inorganic hydroxyl groups lying at the particle surface that are similar to the surfaces of pure oxide systems. In areas like the northeastern part of North America, time has not been sufficient, since the last glaciation, to allow an equivalent amount of weathering of the primary minerals in these soils compared to those of the Tropics (Jackson et al., 1948). In these young soils, 2:1 clay phyllosilicates and primary minerals are dominant. This situation explains the difference in surface chemistry of

these soils compared to that of Oxisols; there is a dominance of permanent charge in the former compared to variable charge There are, of course, exceptions such as in in the latter. some podzolic soils that may be poor in 2:1 phyllosilicates. In Quebec soils, specially agricultural ones, the dominant exchange sites are located at the siloxane plane of the phyllosilicates and are considered to be permanent charge The use of potentiometric titration to measure the sites. surface charge of these soils is unsatisfactory because often there is no cross over point of the titration curves (Hendershot and Lavkulich, 1983). However, we believed that some inorganic hydroxyl groups and organic surface functional groups will contribute to the total charge of the surface, due to organic matter and iron and aluminum oxides.

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Gillman and Uehara (1980) proposed a model in which permanent and variable charge could be measured by a combination of potentiometric titration and ion adsorption determination of the cation exchange capacity of the soil. They used soils rich in metal oxides and kaolinite in which the surface charge was mainly dominated by hydroxyl inorganic groups bound to the solid phase. Recently, Schulthess and Sparks (1986, 1987, 1988) criticized the use of such titrations because they lead to the conclusion that the total concentration of surface functional groups is impossibly high. They proposed a backtitration technique that gives titration curves with inflection points and plateaus that are

specifically attributed to a particular surface reaction. In their development they considered the reaction that involve the dissolution of the solid phase that consume  $H^*$  or  $OH^*$ during the titrations. The idea that there is an error in the titration curves when the solid dissolves was also reported in earlier studies (Parker et al., 1979). Similarly, ion adsorption techniques can lead to unusual results when the pH is below 5 (Bolland et al., 1976, Duquette and Hendershot, 1987). Models based on laboratory experiments must have an appropriate procedure that takes into account dissolution reactions and the speciation of ions in solution. This is particularly true for some podzolic soils of glaciated areas where the amorphous Al oxides are not stable and dissolve rapidly when the pH of the soil is reduced below field pH. Also, as discussed in the preceding chapter, a multisite adsorption model should give a better representation of the surface charge of soils than surface complexation models based on multiple layers.

In this paper a titration procedure is proposed for the determination of the pH-dependent surface charge of soils with either a dominance of 2:1 clay phyllosilicates, or a solid phase that is soluble at low pH. This procedure takes into account the solubility of the solid phase and the dissolved ions in the calculation of surface charge by titration.

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At every point during the potentiometric titration of a solid the electroneutrality of the suspension is maintained:

 $\Sigma$ (negative charges) =  $\Sigma$ (positive charges) [2.1] In a titration of a suspension with Ca(OH)<sub>2</sub> or HNO<sub>3</sub> as titrant and in a background electrolyte solution of Ca(NO<sub>3</sub>)<sub>2</sub>, the electroneutrality equation can be written:

[OH'] + [NO<sub>3</sub>'] + [=SO'] = [H'] + 2[Ca<sup>2+</sup>] + [=SOH<sub>2</sub>\*] [2.2] Where [] indicates concentration in mole L<sup>-1</sup>, [=SO'] and [=SOH<sub>2</sub>\*] the concentration of negative and positive surface sites in mol<sub>c</sub> L<sup>-1</sup>. In equation 2.2, it is assumed that no dissolution occurs during the titration. In the case of pure oxide systems that have been purified before surface charge measurement, equation 2.2 can be applied without further consideration. In soils where soluble compounds are present, partial dissolution of the solid phase will release ions into solution that will contribute to the electroneutrality of the suspension. This was observed by Parker et al. (1979), where the amount of Al dissolved gave erroneous surface charge values when Al and it hydroxo complexes were not taken into account in the surface charge balance. In this case, equation 2.2 must be modified to the following:

 $[OH^{-}] + [NO_{3}^{-}] + [\equiv SO^{-}] + \Sigma z_{2}[A^{2^{-}}] =$   $[H^{+}] + 2[Ca^{2^{+}}] + [\equiv SOH_{2}^{+}] + \Sigma z_{4}[C^{2^{+}}] \qquad [2.3]$ 

Where [A<sup>2\*</sup>] is the concentration of other anions and

oxyanions in solution and  $[C^{2+}]$  is the concentration of cations and positive hydroxo complexes of cations other than those forming the electrolyte solution. By definition:

$$[H^{+}] = 10^{-pH} \text{ and } [OH^{-}] = 10^{pH-pW}$$
 [2.4]

(Schulthess and Sparks, 1986) and pW is the negative log of the self-ionization constant of water,

$$[NO_{3}] = [HNO_{3}]_{added} + 2[Ca(NO_{3})_{2}]_{added}$$
 [2.5]

and

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$$[Ca^{2+}] = [Ca(OH)_2]_{added} + [Ca(NO_3)_2]_{added}$$
 [2.6]

If the concentrations are expressed in normality instead of molarity,

$$[NO_{3}^{-}] - 2[Ca^{2+}] = N_{HNO3} + N_{Ca(NO3)2} - N_{Ca(OH)2} - N_{Ca(NO3)2} [2.7]$$
$$[NO_{3}^{-}] - 2[Ca^{2+}] = N_{HNO3} - N_{Ca(OH)2} [2.8]$$

When dissolution occurs during titration, releasing ions that can hydrolyze in solution, the resulting equation of the H'/OH' consumption, "Q", of a suspension, can be expressed, by rearranging equation 2.3, as:

$$Q^* = [=SOH_2^*] - [=SO^*]$$
 [2.9]

or

 $Q^* = [OH^-] - [H^+] + [NO_3^-] - 2[Ca^{2+}] + \Sigma z_{-}[A^{2-}] - \Sigma z_{+}[C^{2+}] [2.10]$  $Q^* = [OH^-] - [H^+] + N_{HNO3} - N_{Ca(OH)2} + \Sigma Z_[A^{z^-}] - \Sigma Z_+[C^{z^+}]$ [2.11]

Similarly, the H\*/OH consumption "Q" for a non-dissolving solid can be written as :

 $Q = [\equiv SOH_2^+] - [\equiv SO^-] = [OH^-] - [H^+] + N_{HNO3} - N_{Ca(OH)2}$ [2.12]Similarly, the surface charge " $\Gamma$ " and " $\Gamma$ <sup>\*</sup>" in cmol<sub>c</sub> kg<sup>-1</sup>

can be written as:

$$\Gamma(\Gamma^*) = Q(Q^*)/a$$
 [2.13]

Where,  $a = 100 (cmol_{c} mol_{c}^{-1}) / particle concentration (kg L<sup>-1</sup>). The pH<sub>PZNPC</sub> is defined as the pH at which the net surface charge by adsorption of H<sup>+</sup> is zero (Sposito, 1981). The pH<sub>PZNPC</sub> whether dissolution occurs or not will be:$ 

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 $\Gamma = 0 = ([OH^{-}] - [H^{+}] + N_{HNO3} - N_{Ca(OH)2})/a \qquad [2.14]$  $\Gamma^{*} = 0 = ([OH^{-}] - [H^{+}] + N_{HNO3} - N_{Ca(OH)2}$ 

+ 
$$\Sigma z_{A^{2}} - \Sigma z_{C^{2}}/a$$
 [2.15]

At any point in the titration for a dissolving solid, the difference between the true surface charge and the apparent surface charge will be:

$$\Gamma - \Gamma^* = (-\Sigma z_{[A^{2^*}]} + \Sigma z_{+}[C^{2^*}])/a \qquad [2.16]$$

When working with pure oxides that have been treated to remove impurities equation 2.14 can be applied. In the case of soils that possess a soluble solid phase, the true surface charge must be corrected for the anionic and cationic species in solution that result from the dissolution of the solid. The problem with the potentiometric titration method is the evaluation of the value of  $-\Sigma z [A^{2^{-}}] + \Sigma z_{*}[C^{2^{+}}]$  at each titration step. If batch titration is done, it is always possible to measure this value and to calculate the balance for the electroneutrality equation in each solution. However, in continuous titration it is impossible to analyze all the ions at each titration step, unless a small amount of solution is removed each time.

#### 2.3 Oxides Versus Soils

In the surface charge evaluation of oxides some assumptions are usually made. First, the H<sup>+</sup> or OH<sup>-</sup> removed from the solution during the titration is consumed only through surface protonation and no H<sup>+</sup> or OH<sup>-</sup> reacts with the electrolyte background solution. Secondly, the solid does not dissolve during the titration, and finally the electrolyte solution is considered as indifferent. The last assumption has been criticized recently because by definition all ions have an affinity, even if small, for a charged surface (Schulthess and Sparks, 1989; Gibb and Koopal, 1990).

During titration of soils the following reactions occur: 1. When the pH of a soil suspension is different than the original (or field) pH, some solid phases are likely to release ions into solution. Even at soil pH, some dissolution can occur.

- 2. Proton and OH<sup>-</sup> consumption during the titration will be a function of: (1) the protonation reaction at the surface, (2) dissolution/precipitation reactions and (3) hydrolysis reactions of dissolved ions through the formation of metallic hydroxo-complexes.
- 3. The H<sup>+</sup> and OH<sup>-</sup> will react with multiple surface functional groups in soils, i.e. organic and inorganic surface functional groups from different minerals.

If the objective of the titration is to measure the amount and sign of the variable charge (Qv) in the soil, the titration curve must be corrected for the ions dissolved. Consequently,

 $\Gamma = f(Qv) + f(dissolution/precipitation, hydrolysis)$  [2.17] and for soils the variable surface charge can be defined as:

 $\Gamma = Qv = \Gamma^* - (\Sigma z_{-}[A^{z^*}] + \Sigma z_{+}[C^{z^*}])/a \qquad [2.18]$ 

If the net surface charge in soils is measured by ion adsorption and no dissolution occurs, the pH-dependent surface charge determined by ion adsorption must be equal to that measured by potentiometric titration. If the surface charge determined by potentiometric titration has not been corrected for dissolution and hydrolysis reactions, then the two pHdependent surface charge measurements will be different by an amount approximately equal to the H<sup>+</sup>/OH<sup>-</sup> consumed by dissolution and hydrolysis reactions. By using the equations described above with potentiometric titration, we should be able to obtain a good fit of the pH-dependent surface charge measured by ion adsorption and potentiometric titration.

### 2.4 Backtitration Model

A backtitration technique was developed recently by Schulthess and Sparks (1986, 1987, 1988, 1989) for the evaluation of the surface charge of oxides. This technique has the advantage that the dissolution of the solid phase is

taken into account and that the surface charge measured as a function of pH is represented by a series of inflection points and plateaus that can be associated with different surface reactions. It appears that their technique worked well when applied to oxides, but it has not yet been tested with soils. This method is also time consuming because it involves the backtitration of each solution after the addition of base or acid.

The purpose of this section is to propose a relatively fast titration method that will provide a good correlation between the pH-dependent charge measured by ion adsorption and potentiometric titration for soils of glaciated areas. It is assumed in this titration procedure that the soils have very low anion exchange capacity, consequently all the protonation reactions involve only surface functional groups that are either neutral (=SOH) or negatively charged (=SO'). The sample titration proceeds as follows: A suspension is equilibrated in an electrolyte solution until the pH remains constant. Then the pH is gradually decreased to 3 by stepwise addition of acid and then backtitrated to pH 8 or 10. In the first part of this method, the decrease in pH corresponds to a normal titration and the H<sup>+</sup> consumption is due to both protonation reactions and dissolution/hydrolysis reactions. Similarly the sample backtitration will involve the following reactions:

i) Surface Reactions:  $\equiv$ SOH + OH  $\Rightarrow \equiv$ SO<sup>+</sup> + H<sub>2</sub>O

ii) Hydrolysis Reactions: xMe<sup>2+</sup> + yOH<sup>-</sup> → Me<sup>2+</sup>,(OH),<sup>(x2-y)+</sup>

iii) Any unknown reactions in the solution during base titration.

Reference titration is required to correct for the H\*/OH consumption in a given electrolyte solution. The reference titration proceeds as follows: Using the same amount of soil and electrolyte as for the first titration the suspension is equilibrated at its natural pH and then the pH is decreased to 3 in the same way as before, with the same titration rate. Once pH 3 is reached, the suspension is centrifuged and the supernatant solution is transferred into a new titration cell and backtitrated as described above. The resulting OH<sup>-</sup> consumption during the reference backtitration will be due to: i) Hydrolysis Reactions:  $xMe^{2+} + yOH^- \rightarrow Me^{2+}_{x}(OH)_{x}^{(x2-y)+}$ 

ii) Any unknown reactions in solution during base titration.

The OH consumed by both the reference and the sample titrations can be calculated as follow:

$$\Gamma_{\text{sample}} = a \times (N_{\text{base}} \times V_{\text{sample}} / W_{\text{soil}}) \qquad [2.19]$$

and

 $\Gamma_{\text{reference}} = a \times (N_{\text{base}} \times V_{\text{reference}} / W_{\text{soil}}) \times (V_{\text{o}}/V_{\text{sn}}) \quad [2.20]$  Where,

$$\begin{split} &\Gamma_{\text{sample}}: \text{ OH consumed by the sample, } \text{cmol}_{\text{c}} \text{ kg}^{-1}. \\ &\Gamma_{\text{reference}}: \text{ OH consumed by the reference solution, } \text{cmol}_{\text{c}} \text{ kg}^{-1}. \\ &N_{\text{base}}: \text{ Normality of the base used to backtitrate.} \\ &V_{\text{sample}}: \text{ Volume of base added during the sample titration, mL.} \\ &V_{\text{reference}}: \text{ Volume of base added during the reference} \end{split}$$

titration, mL.

V<sub>o</sub>: Initial volume, mL. V<sub>o</sub> = Volume of electrolyte added + volume of acid required to decrease the pH down to 3 at the beginning of the titration, before backtitrating.
V<sub>sn</sub> : Volume of the supernatant titrated, (reference), mL.
W<sub>soil</sub> : Weight of the soil, g.

a : Correction factor for unit conversion, a=100.

 $(a = 1000 \text{ g kg}^{-1} \times 0.001 \text{ L mL}^{-1} \times 100 \text{ cmol}_{c} \text{ mol}_{c}^{-1})$ 

The surface charge due to pH-dependent surface functional groups is then calculated by subtracting the reference from the sample titration.

 $\Gamma_{surface} = \Gamma_{sample} - \Gamma_{reference}$ , at each pH value. [2.21] To calculate the variation of the total CEC as a function of pH we need to know the total CEC at a given pH. This can be done by determining the total CEC by using an ion adsorption method (Fey and LeRoux, 1976) at a pH close to the soil pH. It is important to use a value for the total CEC close to the soil pH, because it is expected that at this pH value dissolution will be at a minimum.

#### 2.5 Expected Results

By using this technique it is possible to cancel out the effect of the soluble ions that contribute to OH<sup>-</sup> consumption during the backtitration. By subtracting the reference titration from the sample titration it is possible to obtain

a measurement of the OH interaction with the surface. Figure 2.1 presents a typical result of the backtitration curves for the sample, the reference backtitration and the resulting curve for the OH consumption by the surface of an Ap horizon of a gleysolic soil (Rideau series). The curve for the surface is assumed to be due only to the OH consumed by the pH-dependent surface functional groups. However, two errors could occur in the attribution of the OH' only to surface consumption in this curve. First, we assume that only amphoteric species in solution or pH-dependent surface functional groups react. If, during the lowering of the pH, there is H<sup>\*</sup> adsorption at the ditrigonal siloxane plane of the 2:1 clay phyllosilicates, the OH consumption during the titration could be due in part to H\* desorption from this surface group. The second problem is the adsorption and precipitation of ions such Al<sup>3+</sup> onto the surface during the backtitration of the sample, but absent in the reference backtitration. During the backtitration, if there is an excess of  $Al^{3+}$  or  $Fe^{3+}$  in solution at the beginning of the backtitration, it is possible that during the sample titration, part of the OH consumption will be due to the adsorption, hydrolysis and precipitation of the Al3+ at the surface of soil particles. In this case, the total OH consumption, even with the reference titration, could not be corrected for this reaction.



Figure 2.1 Sample, reference and the resulting backtitration for the Ap horizon of the Rideau soil.

With the exception of these two side reactions, the final titration curves will measure the OH<sup>-</sup> consumption of the surface. With the proposed method it will be possible to apply a surface charge model like those derived for oxides to the data for temperate region soils.

#### 2.6 Data Interpretation

In this model, the pH-dependent backtitration curve consists of a series of inflection points and plateaus, reflecting different types of sites according to the following

reaction:

$$\equiv S_{(i)}OH \iff \equiv S_{(i)}O^{-} + H^{+} \qquad [2.22]$$

where the subscript "i" refers to the site number. Here, it is necessary that the distinction between sites and surface functional groups must be defined. In this text and in the following discussion, the surface functional groups keep the same definition as described in Chapter I while a site is considered as one or more soil component that generate surface charge over a given range of pH, i.e. organic matter, metalorganic complex, etc.

By the technique described above, a series of equilibrium constants  $(K_{(i)})$  and total surface charge of sites  $(Qm_{(i)})$  can be determined. It is assumed that the total pH-dependent charge is the result of the contribution of different surface sites (i). Each site has its own equilibrium constant and responds to a Langmuir type isotherm for H<sup>+</sup>/OH<sup>-</sup> adsorption. Consequently, the following equations can be used to model the backtitration curve. Each site will have the following properties:

$$Qv_{(i)} = K_{(i)}Qm_{(i)}/(K_{(i)}+[H^+])$$
 [2.23]

Where  $Qv_{(i)}$  and  $Qm_{(i)}$  are in  $cmol_c$  kg<sup>-1</sup>. The total pH-dependent CEC (Qv) can be computed by the following equation:

 $Qv = \Sigma Qv_{(i)} = \Sigma (K_{(i)}Qm_{(i)}/(K_{(i)}+[H^{+}])), \text{ for } i=1,2,3,..$  [2.24]

Figure 2.2 shows a theoretical pH-dependent surface charge curve. In this Figure, each inflection point will represent one  $K_{(i)}$ . This curve has been obtained for a three
### site model using the following data;

| site | number | pK <sub>(i)</sub> | Qm <sub>(i)</sub> |
|------|--------|-------------------|-------------------|
|      | 1      | 4.20              | 12.0              |
|      | 2      | 6.45              | 5.0               |
|      | 3      | 8.50              | 18.5              |



Figure 2.2 Surface hydroxyl consumption curve (theoretical).

It is sometimes difficult to detect the exact location of the inflection points on the curve. An alternative method to solve this problem is to plot the first derivative of this curve (dQv/dpH) against pH or against Qv (Figures 2.3 and 2.4). It can be seen on Figure 2.3 that there are three



Figure 2.3 dQv/dpH versus pH (theoretical).

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maxima, one at each pK<sub>(i)</sub>. Using this method with the same value for Qm, two pK's farther apart than about 2 pH units will be easily located, while when they are closer than 1 pH unit, only one pK will be detected and the pK will appear to be an average of the two. Similarly, in Figure 2.4 the three maxima now correspond respectively to:

max. #1 0.5  $Qm_{(1)}$ max. #2  $Qm_{(1)}$  + 0.5  $Qm_{(2)}$ max. #3  $Qm_{(1)}$  +  $Qm_{(2)}$  + 0.5  $Qm_{(3)}$ 

By analyzing graphically these curves it is possible to calculate the pH-dependent CEC as the summation of individual sites. A backtitration of soil suspensions should give



Figure 2.4 dQv/dpH versus Qv (theoretical).

> similar results. If so, it will be possible to attribute to each site the type of soil component that controls the variable charge over a given range of pH, i.e. organic matter, Al and Fe organic complexes or amorphous materials.

> It is believed that in soils it will be possible to correlate these sites with specific chemical compounds such as the amount of organic matter, or Al and Fe extractable by Napyrophosphate or  $NH_4$ -oxalate. These compounds are believed to be responsible for the pH-dependent CEC (Evans, 1982; Duquette and Hendershot, 1987).

#### 2.7 Conclusion

In this chapter, a new method was proposed for the measurement of pH-dependent surface charge of a soil. The use of acid addition followed by backtitration will result in a pH-dependent surface charge curve corrected for dissolved ions and other chemical reactions in solution interfering with the OH<sup>-</sup> consumption measurement at the surface. Two assumptions must be made for the method to be valid; (1) the soil does not possess a significant anion exchange capacity and (2) the effect of adsorption-precipitation and hydrolysis of  $Al^{3*}$  and  $Fe^{3*}$  at the surface of the soil during the sample backtitration is negligible.

From the resulting data, and an appropriate graphical representation, it is possible to detect a number of types of sites contributing to the pH-dependent surface charge. These sites can be characterized by an equilibrium constant for surface ionization and a maximum amount of surface charge governed by the Langmuir isotherm.

Contrary to the surface complexation models that are based on a diffuse layer definition, this model proposes that the total surface charge of the soil arises from various chemical or mineralogical compounds. This assumes that multisite adsorption of  $H^*/OH^*$  seems more realistic than multi layers of adsorption. It is evident that this model is in the development stage and an improvement could be obtained if each

site was modelled individually using a multi-layer adsorption sub-model.

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## CHAPTER III

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# EVALUATION OF THE SURFACE CHARGE OF CLAYS, SOILS AND OXIDES.

II. APPLICATION.

3.0 Evaluation of the Surface Charge of Clays, Soils and Oxides. II. Application

#### 3.1 Introduction

Two methods are commonly used for the determination of surface charge in soils; potentiometric titration and ion adsorption. The former usually assumes that only variable surface charge is measured while the latter measures both the variable and permanent surface charge (Gillman and Uehara, 1980). Since the work of van Raij and Peech (1972) potentiometric titration is commonly used to assess variable surface charge of soils.

The results obtained from potentiometric titration are the basis of the development of the surface complexation models which are based on different concepts of the structure of the diffuse double layer. In contrast, the model presented in this chapter is based on the concept that there are different materials controlling the variable charge; this is termed a multisite model. A site is defined as being a soil component possessing either one or more organic or inorganic surface functional groups, capable of generating surface charge. The choice of a multisite model is based on the following arguments. It is often recognize that oxyanion adsorption in soil can fit a two-site Langmuir equation rather than a one-site equation (Juo and Maduakor, 1974; Sposito, 1982; Kinniburgh, 1986). This implies that there are: (1) two soil minerals, (2) two types of surface functional group or (3) two types of site involved in the sorption process. Thus it seems unreasonable to use a single site equation to described H<sup>+</sup> adsorption in soil when it is thought the surface charge is generated by a complex chemical and mechanical mixture of materials.

In two recent papers by Hiemstra et al. (1989a, 1989b) it was found that the surface charge of hydroxides and oxides could be modelled by using a multisite proton adsorption model. This observation comes from the fact that the surface of oxides is composed of different crystalline planes having specifically either singly, doubly or triply metal coordinated surface functional groups, and on each of these groups protonation of the oxo ( $\equiv$ SO<sup>+</sup> + H<sup>+</sup>  $\rightarrow \equiv$ SOH) or hydroxo ( $\equiv$ SOH + H<sup>+</sup>  $\rightarrow \equiv$ SOH<sub>2</sub><sup>+</sup>) complexes can occur. The model presented in these papers was successful from both a theoretical and practical point of view in modelling of surface charge of various oxides.

A multisite approach for pure oxides is relatively easy to develop as it is to perform the laboratory analysis necessary to confirm the model. For soil, the situation is quite different. Even if the adsorption of heavy metals on oxides can be explained by the difference in affinity of one metal for a particular surface functional group (Benjamin and Leckie, 1981a, 1981b), the adsorption in soils will be more a

function of the different minerals than a function of the different planes of one particular mineral.

It is expected that in soils  $H^{+}$  adsorption will be a function of the surface of the minerals in contact with the equilibrium solution. In a podzolic soil the accumulation of the organo-metallic complexes of Al and Fe will exert a large influence on the surface charge because they form coatings around soil particles. Organic matter (fulvic and humic acid) adsorbed on clay mineral particles will also control the H\* adsorption isotherm. Because these compounds form a coating around the soil particles, the apparent pK of the equilibrium reaction between an H<sup>+</sup> ion and the surface would be different than the pK's determined for either the particle or the coating material. For example, the titration of humic (HA) and fulvic acid (FA) will not give the same inflection points as the titration of these organic acids adsorbed on the surface of a clay mineral or oxide (Davis, 1982). This can be visualized by assuming that at least one type of surface functional group of the organic matter must form a complex, either by cation exchange, protonation, anion exchange, etc. with the surface of the clay mineral (Sposito, 1984). In this case, some of the surface functional groups initially present in the organic fraction are neutralised and some others are involved in the H<sup>+</sup> adsorption isotherm.

The objective of this study is (1) to test the backtitration method as described in chapter II for some

gleysolic and podzolic soils of Quebec and (2) to evaluate by statistical means which soil components are responsible for the different variable charge sites in these soils.

#### 3.2 Materials and Methods

Ten horizons from five soils located in different parts of Quebec were used to test the backtitration method. The Ap and Bg horizons from three Orthic Humic Gleysols from the St-Lawrence Lowlands, named Ste-Rosalie, Rideau and St-Urbain series, the Bfl and the IIBm from an Orthic Humo-Ferric Podzol located in the Ungava Peninsula and the Bhf and Bf horizons from an Orthic Humo-Ferric Podzol located in the Lower Laurentians. The samples were air-dried and particles > 2 mm removed.

#### 3.2.1 Soil Characterization

Exchangeable cations were determined by the  $BaCl_2$  method of Hendershot and Duquette (1986). Specific surface area of the samples was measured using the ethylene glycol monoethyl ether (EGME) method (Eltantawy and Arnold, 1973). Organic carbon was analysed by the Walkley-Black wet digestion method. Soil pH was measured in H<sub>2</sub>O and 0.01 M CaCl<sub>2</sub> using a soil to solution ratio of 1:1 and 1:2 respectively. Sodium pyrophosphate and NH<sub>2</sub>-oxalate extractable Fe and Al were

determined following the procedures of McKeague (1978). X-ray diffraction analysis was performed on the clay fraction (< 2  $\mu$ m) using orientated-aggregate slides in the Mg, Mg-ethylene glycol, KCl air-dried, and KCl heated to 300°C and 550°C states (Whittig, 1965). The percentage of clay was determined using the pipet method (McKeague, 1978).

#### 3.2.2 Ion Adsorption

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A method similar to that of Fey and LeRoux (1976) was used to determine the surface charge of the samples, using  $Ca^{2+}$ and NO, as the index ions and K\* and Cl as the replacing Five hundred mg of sample were weighed into 100 mL ions. polyethylene beakers to which were added 40 mL of 1 M  $Ca(NO_3)_2$ saturating solution, previously adjusted to pH 3, 4, 5, 6, 7 or 8 with HNO, or Ca(OH),. The pH of each suspension was readjusted after 2, 6 and 16 h. The suspensions were then transferred into screwcap 50 mL polyethylene centrifuge tubes and five washing steps were performed with 0.1 M Ca(NO3), saturating solutions at the desired pH. Then four washing steps using 1 M KCl were used to remove the adsorbed Ca<sup>2+</sup> and NO3; these supernatants were collected in 100 mL volumetric The  $Ca^{2+}$  and  $NO_{3}^{-}$  displaced by the KCl salt were flasks. analysed by atomic absorption spectrometry and colorimetry (Keeney and Nelson, 1982) respectively. Adsorbed monomeric Al was also measured in these solutions by the oxine method

(James et al., 1983; Lalande and Hendershot, 1986). The AEC and CEC were calculated after correction for the concentration of  $Ca^{2+}$  and  $NO_3^-$  in the occluded soil solutions.

#### 3.2.3 Basic Backtitration

The sample backtitration was performed as follows: 1 g of soil was weighed into a 100 mL beaker. Then 40 mL of electrolyte solution (0.1 M Ca(NO3)) was added and the suspension was stirred until constant pH was obtained. The suspension was then titrated with 0.1 mL of standardized 0.1 M HNO3 with two min equilibrium periods between each addition, until a pH of 3 was reached. The suspension was then backtitrated with standardized 0.005 M Ca(OH), at a titration rate of 0.4 mL per min to pH 10. The pH was recorded on a chart recorder during this time. The reference titration was the suspension was prepared and performed as follows: titrated to pH 3 as described above. Then the suspension was transferred into a pre-weighed 50 mL centrifuge tube and centrifuged (15 min, 2500 rpm). The supernatant was filtered (polycarbonate 0.4 µm), weighed and transferred into a 100 mL beaker. The supernatant solution was allowed to equilibrate 10 min while continuously stirring the solution. Then the solution was backtitrated as described above. The surface charge due to hydroxyl consumption was calculated by subtracting the OH consumption of the reference from the

sample backtitration at the same pH. Each curve calculated from these data represents a continuum of sixty to seventy individual titration points. For the gleysolic soils, sixty to seventy titration points were recorded, while for the podzolic soils forty to seventy titration points were used.

#### 3.2.4 Backtitration Test

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To determine the variability in the results of the basic backtitration technique, a series of backtitrations were performed on a suspension of the Bg horizon of the St-Urbain soil. This horizon was backtitrated in 0.01 M  $Ca(NO_3)_2$  as supporting electrolyte with two soil to solution ratios (1:20, 1:200) and with a backtitration rate of 1 mL or 0.2 mL per min. In each case, the effect of either a 2 min or 16 h. equilibrium period before backtitrating the sample or the reference solution was tested.

#### 3.2.5 Parameter Estimation

To characterize and describe the pH-dependent surface charge, a model was developed to evaluate the values of the log  $K_{(i)}$ 's and  $Qm_{(i)}$ 's. Each soil was analysed separately, and from the observed dQv/dpH plot, four log  $K_{(i)}$ 's were determined graphically from the positions of the maxima. Once each soil was analysed by this method, it was concluded that the pH-

dependent surface charge of all the soils could be modelled using the same four constants for log  $K_{(i)}$ 's. A statistical package (Wilkinson, 1989) was used to evaluate the  $Qm_{(i)}$ parameters.

3.3 Results and Discussion

#### 3.3.1 Sample Characterization

The two Orthic Humo-Ferric Podzols are developed on glacial till with textural class varying between a loam and a sand, while the Ap and the Bg horizons of the three Orthic Humic Gleysols have a clay texture and are developed on marine clay (Table 3.1). For the soil horizons from podzolic soils, all the soil pH values measured in CaCl, are below 5.4, while the gleysolic soils are higher (Table 3.2). The range of extractable Fe and Al, the specific surface area and the organic carbon are as expected for podzolic and gleysolic soils. The podzolic soils have a higher amount of extractable Fe and Al than the gleysolic soils, emphasizing the fact that in these soils the migration of Fe and Al in the form of metal-organic complexes is more pronounced than in the clay soils. Similarly, the specific surface areas of the podzolic soils are lower than the gleysolic soils, where the high amount of clay contributes to higher surface area as measured by the EGME method.

| Sample<br>no. | Soil name or series | Soil<br>Horizon | Classification                | Parent<br>Material | Texture    | Clay<br>% |
|---------------|---------------------|-----------------|-------------------------------|--------------------|------------|-----------|
| 1             | Pin Blanc           | Bhf             | Orthic Humo-<br>Ferric Podzol | Glacial<br>Till    | Sandy Loam | 18.1      |
| 2             | Pin Blanc           | Bf              | Orthic Humo-<br>Ferric Podzol | Glacial<br>till    | Loamy sand | 14.1      |
| 3             | Lac des Moraines    | Bf1             | Orthic Humo-<br>Ferric Podzol | Glacial<br>Till    | Loam       | 7.1       |
| 4             | Lac des Moraines    | I I Bm          | Orthic Humo-<br>Ferric Podzol | Glacial<br>Till    | Sand       | 7.6       |
| 5             | Ste-Rosalie         | Ap              | Orthic Humic<br>Gleysol       | Marine<br>Clay     | Heavy clay | 64.6      |
| 6             | Ste-Rosalie         | Bg              | Orthic Humic<br>Gleysol       | Marine<br>Clay     | Heavy clay | 79.9      |
| 7             | St-Urbain           | Ap              | Orthic Humic<br>Gleysol       | Marine<br>Clay     | Clay       | 51.7      |
| 8             | St-Urbain           | ßg              | Orthic Humic<br>Gleysol       | Marine<br>Clay     | Clay       | 58.9      |
| 9             | Rideau              | Ap              | Orthic Humic<br>Gleysol       | Marine<br>Clay     | Clay       | 55.4      |
| 10            | Rideau              | 8g              | Orthic Humic<br>Gleysol       | Marine<br>Clay     | Heavy clay | 66.1      |

Table 3.1 Soil description.

Table 3.2 Soil chemical properties.

| No | Soil    | Organic | рн    |                             | SSA                            | Pyrop  | hosphate | 0      | Oxalate |  |
|----|---------|---------|-------|-----------------------------|--------------------------------|--------|----------|--------|---------|--|
|    | Horizon | с<br>х  | water | 0.01 M<br>CaCl <sub>2</sub> | m <sup>2</sup> g <sup>-1</sup> | Fe (%) | AL (X)   | Fe (%) | AL (%)  |  |
| 1  | Bhf     | 5.88    | 5.05  | 4.40                        | 98                             | 0.47   | 1.12     | 1.76   | 2.75    |  |
| 2  | Bf      | 3.76    | nd    | 5.31                        | 86                             | 0.17   | 0.77     | 0.77   | 2.07    |  |
| 3  | Bf1     | 3.08    | 4.58  | 4.15                        | 78                             | 0.68   | 0.37     | 0.93   | 0.38    |  |
| 4  | 1 I Bm  | 0.38    | 4.75  | 3.91                        | 25                             | 0.11   | 0.09     | 0.16   | 0.11    |  |
| 5  | Ар      | 3.42    | 6.78  | 6.22                        | 191                            | 0.06   | 0.04     | 0.48   | 0.24    |  |
| 6  | Bg      | 0.45    | 7.48  | 6.56                        | 178                            | 0.02   | 0.00     | 0.40   | 0.27    |  |
| 7  | Ap      | 6.74    | 6.38  | 5.87                        | 107                            | 0.08   | 0.11     | 0.48   | 0.30    |  |
| 8  | Bg      | 0.94    | 7.42  | 6.46                        | 157                            | 0.03   | 0.03     | 0.36   | 0.25    |  |
| 9  | Ap      | 2.78    | 6.58  | 5.98                        | 139                            | 0.06   | 0_04     | 0.78   | 0.27    |  |
| 10 | 89      | 6.27    | 6.27  | 5.46                        | 186                            | 0.05   | 0.03     | 0.72   | 0.25    |  |

Aluminum is the major exchangeable cation of the podzolic horizons, contributing to more than 50 % of the effective cation exchange capacity of these soils (Table 3.3). For the agricultural soils,  $Ca^{2+}$  and  $Mg^{2+}$  are the dominant ions with a cation exchange capacity of 20  $cmol_c$  kg<sup>-1</sup> or more compared to the podzolic horizon where the cation exchange capacity is lower than 5  $cmol_c$  kg<sup>-1</sup> at field pH values.

On the basis of mineralogical analysis the soil samples can be described as follow (Table 3.4). The podzolic samples (#3 and #4) from the Ungava Peninsula contain vermiculite, quartz and kaolinite as the most abundant minerals in the clay fraction, while the podzol from the Lower Laurentians (#1 and #2) is dominated by quartz and is very low in 2:1 clay phyllosilicates (Table 3.4). The gleysolic soils (#5 to #10) are either dominated by vermiculite or mica and are soil horizons rich in 2:1 clay phyllosilicates inherited from the marine clay deposit.

#### 3.3.2 Backtitration Data

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The OH<sup>-</sup> consumption curves for the sample and reference backtitrations of the Ap horizon of St-Urbain soil are shown in Figure 3.1. The resulting OH<sup>-</sup> consumption by the surface is also shown. These curves for the other samples are similar and only this sample is shown. The average standard deviation in the titration results is about 0.5 to 1 cmol<sub>c</sub> kg<sup>-1</sup>. In the

| No | Soil    |                   | Exchangeable Cations (cmol <sub>c</sub> kg <sup>-1</sup> ) |      |      |      |      |      |      | рН <sup>(1)</sup> |
|----|---------|-------------------|------------------------------------------------------------|------|------|------|------|------|------|-------------------|
|    | Horizon | AL                | Fe                                                         | Mn   | Ca   | Na   | ĸ    | Mg   |      | <u> </u>          |
| 1  | Bhf     | 1.12              | 0.06                                                       | 0.01 | 0.70 | 0.03 | 0.05 | 0.07 | 2.04 | 4.20              |
| 2  | Bf      | 0.97              | 0.03                                                       | 0.01 | 0.61 | 0.06 | 0.04 | 0.17 | 1.89 | 5.31              |
| 3  | Bf1     | 3.18              | 0.40                                                       | 0.01 | 0.58 | 0.07 | 0.03 | 0.22 | 4.49 | 4.01              |
| 4  | IIBm    | 0.76              | 0.12                                                       | 0.00 | 0.15 | 0.03 | 0.01 | 0.05 | 1.12 | 4.28              |
| 5  | Ар      | nd <sup>121</sup> | nd                                                         | nd   | nd   | nd   | nd   | nd   | nd   | nd                |
| 6  | Bg      | 0.00              | 0.04                                                       | 0.03 | 25.7 | 0.40 | 0.49 | 6.52 | 33.2 | 6.22              |
| 7  | Ар      | 0.00              | 0.20                                                       | 0.60 | 24.6 | 0.36 | 0.84 | 6.56 | 33.1 | 5.59              |
| 8  | Bg      | 0.00              | 0.20                                                       | 0.20 | 15.2 | 0.61 | 0.30 | 6.28 | 22.8 | 5.89              |
| 9  | Ap      | 0.00              | 0.19                                                       | 0.70 | 20.4 | 0.33 | 0.38 | 7.50 | 29.5 | 5.65              |
| 10 | Bg      | 0.00              | 0.19                                                       | 0.20 | 15.2 | 0.49 | 0.41 | 9.65 | 26.5 | 4.96              |

# Table 3.3 Exchangeable cations and CEC.

(2): nd : not determined

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# Table 3.4 Mineralogy of the clay fraction.

| No    | Horizon                                          | Mica | Quartz | Vermiculite | Chlorite | Kaolinite | Feldspars | Amphiboles |  |
|-------|--------------------------------------------------|------|--------|-------------|----------|-----------|-----------|------------|--|
| 1     | Bhf                                              |      | ***    |             |          |           |           |            |  |
| 2     | Bf                                               |      | ***    |             |          |           |           | **         |  |
| 3     | Bf1                                              |      | ***    | ****        | **       | ***       | *         | **         |  |
| 4     | IIBm                                             |      | ***    | ****        | **       | ***       | **        | ***        |  |
| 5     | Ap                                               | ***  | **     | ****        | *        |           | **        |            |  |
| 6     | Bg                                               | ***  | **     | ***         |          | *         | **        | *          |  |
| 7     | Ap                                               | ***  | **     | ****        | ***      |           | **        | **         |  |
| 8     | Bg                                               | ***  | **     | ****        | **       |           | **        | **         |  |
| 9     | Ap                                               | ***  | **     | ****        |          |           | **        |            |  |
| 10    | Bg                                               | **** | **     | ***         |          |           | **        |            |  |
| * tra | * trace; ** present; *** abundant; **** dominant |      |        |             |          |           |           |            |  |



Figure 3.1 Sample, reference and the resulting surface backtitration curves for the Ap horizon of the St-Urbain soil.

backtitration curve it is difficult to observe the series of inflection points and plateaus. The only inflection point that could be detected visually in all the samples is in the reference backtitration and the resulting surface OH consumption curve.

Figures 3.2A, B and C present the results of the pHdependent surface charge and total CEC measured respectively by the backtitration technique and the ion adsorption method of Fey and LeRoux (1976) for the gleysols. For each soil, the backtitration curve has been adjusted to a known value of the CEC near the field pH of the soil. If we accept the standard error in the surface charge measured by the ion adsorpt on



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Figure 3.2 CEC measured by ion adsorption  $(\Box,\diamond)$  and by the backtitration technique (----) for all soils: (A) Ste-Rosalie; (B) St-Urbain; (C) Rideau; (D) Pin Blanc; (E) Lac des Moraines.

method, the pH-dependent CEC curves measured by both methods agree fairly well. Figure 3.2D presents the data for the Bf and Bhf horizons of the Pin Blanc soil. Compared to the gleysols, the pH-dependent surface charge of the Pin Blanc soil measured by the backtitration technique seems to underestimate the values at high pH; assuming that the ion adsorption measurement represents the true value of the CEC. In general, good agreement is obtained between the two methods. Figure 3.2E shows the results for the Lac des Moraines soil. Again, the pH-dependent charge is well correlated at low pH but divergence occurs at high pH.

#### 3.3.3 Backtitration Test

A backtitration test was performed on the Bg horizon of the St-Urbain soil to verify the variation of the pH-dependent charge as a function of the soil to solution ratio, the equilibrium time before backtitration and the titration rate. The different backtitration curves, in the pH range 3 to 8, are presented in Figure 3.3. All the backtitration curves have a similar shape. At low soil to solution ratio (1:200) the curves are not identical; titration rate and equilibrium time result in different curves. When a soil solution ratio of 1:20 is used the curves are nearly identical.

Table 3.5 presents the results of the pH-dependent CEC, calculated by the difference between pH 8 and 3. Delta CEC values do not change markedly by varying the different titration parameters. However, the standard deviation in the titration is lower when a soil to solution ratio of 1:20 is used. The titration rate affects to a small extent the delta CEC measured, being greater for the slow  $(0.2 \text{ mL min}^{-1})$  than for the fast titration rate (1 mL min<sup>-1</sup>). Maintaining the suspension at pH 3 for 2 min or 16 h does not significantly affect the pH-dependent charge measured. This is a good indication that if dissolution is greater after 16h, the reference titration will correct for the difference in the amounts of dissolved ions in solution subject to hydrolysis reactions.



Figure 3.3 Backtitration curves, for surface charge, at different soil to solution ratios, titration rates and equilibrium time before backtitrating.

Table 3.5 Effect of titration rate, equilibrium time and soil to solution ratio on the pH-dependent CEC (cmol, kg<sup>-1</sup>) of the Bg horizon of the St-Urbain soil (mean  $\pm$  standard deviation, n=2).

|               | Soil:Solution ratio                                    |               |              |              |                |              |              |  |  |  |
|---------------|--------------------------------------------------------|---------------|--------------|--------------|----------------|--------------|--------------|--|--|--|
|               | 1:                                                     | 200           |              |              | 1:             | 20           |              |  |  |  |
|               | Equilibrium Time                                       |               |              |              |                |              |              |  |  |  |
| 2             | min                                                    | 16            | <u>h.</u>    | <u> </u>     | in             | 16 h.        |              |  |  |  |
|               |                                                        |               | Titration    | Rate (mL min | <sup>1</sup> ) |              |              |  |  |  |
| 1             | 0.2                                                    | 1             | 0.2          | 1            | 0.2            | 1            | 0.2          |  |  |  |
|               | pH-dependent CEC in cmol <sub>c</sub> kg <sup>-1</sup> |               |              |              |                |              |              |  |  |  |
| 9_23<br>±4.33 | 10.2<br>±2.5                                           | 9.82<br>±3.02 | 13.5<br>±1.0 | 10_4<br>±0.9 | 11.4<br>±0.2   | 10.7<br>±0.3 | 12.4<br>±0.1 |  |  |  |

#### 3.3.4 Solution Analysis

Table 3.6 presents the data for the analysis of the supernatant solutions separated from suspensions titrated to pH 3. For the ions  $K^*$ ,  $Na^*$ ,  $Mg^{2*}$  and  $Fe^{3*}$  their concentrations in solution are approximately equal to their concentrations as saturating cations on the exchange sites prior to titration. For the gleysols,  $Mn^{2*}$  is released in an amount four times greater than the amount originally adsorbed, indicating that dissolution of  $Mn^{2*}$  compounds occurs when the pH is decreased. Soluble  $Si^{4*}$  was found to be released from all samples. However, more  $Si^{4*}$  was released by the gleysols than the podzols.

Total and monomeric Al were also analyzed. In all cases except for the Lac des Moraines samples, Al was dissolved from the solid phase in excess of the amount adsorbed initially. The polymers of Al, as calculated by the difference between the total and monomeric Al, are insignificant in solution (< 10 % of total dissolved Al) when the standard deviation of the analysis is taken into account.

#### 3.3.5 Parameter Estimation

The pH-dependent surface charge data were plotted in the form of dQv/dpH against the pH to detect maxima in the curve (Chapter II and Figure 3.4) The first derivative plots for

Table 3.6 Solution analysis before backtitrating (mean  $\pm$  standard deviation, n = 2).

| no. | Horizon | рH                             | Al total<br>mmole kg <sup>1</sup> | Al monomeric<br>mmole kg <sup>-1</sup> | Fe<br>mmole kg <sup>-1</sup> | K<br>mmole kgʻ <sup>1</sup> |
|-----|---------|--------------------------------|-----------------------------------|----------------------------------------|------------------------------|-----------------------------|
| 1   | Bhf     | 3.10 ± 0.00                    | 18.7 ± 0.0                        | 18.9 ± 0.4                             | 0.37 ± 0.01                  | 1.85 ± 0.03                 |
| 2   | Bf      | 3.09 ± 0.01                    | 13.7 ± 0.1                        | 13.5 ± 0.1                             | $0.14 \pm 0.00$              | 1.67 ± 0.06                 |
| 3   | Bf1     | 3.03 ± 0.01                    | 7.70 ± 0.29                       | 7.53 ± 0.37                            | 1.24 ± 0.01                  | 2.83 ± 0.69                 |
| 4   | IIBm    | 2.95 ± 0.01                    | 3.04 ± 0.22                       | 2.78 ± 0.47                            | 0.64 ± 0.10                  | 4.27 ± 0.31                 |
| 5   | Ap      | 3.12 ± 0.01                    | 10.2 ± 0.2                        | 9.13 ± 0.07                            | 0.17 ± 0.01                  | 9.37 ± 0.23                 |
| 6   | Bg      | 3.06 ± 0.01                    | 14.6 ± 0.1                        | 14.5 ± 0.3                             | 0.26 ± 0.01                  | 7.88 ± 0.07                 |
| 7   | Ap      | 3.11 ± 0.01                    | 8.72 ± 0.76                       | 8.54 ± 0.53                            | 0.23 ± 0.01                  | 10.5 ± 0.2                  |
| 8   | Bg      | 3.12 ± 0.01                    | 12.9 ± 0.4                        | 13.4 ± 0.4                             | 0.58 ± 0.01                  | 6.45 ± 0.23                 |
| 9   | Ap      | 3.09 ± 0.00                    | 8.25 ± 0.38                       | 7.72 ± 0.19                            | 0.13 ± 0.02                  | 6.33 ± 0.01                 |
| 10  | 8g      | 3.07 ± 0.01                    | 8.80 ± 0.40                       | 8.62 ± 0.33                            | 0.14 ± 0.01                  | 7.05 ± 0.02                 |
| no. | Horizon | Min<br>manole kg <sup>-1</sup> | Si<br>mmole kg <sup>-1</sup>      | Hg<br>mmole kg <sup>1</sup>            | Na<br>mmole kg <sup>-1</sup> |                             |
| 1   | Bhf     | 0.04 ± 0.00                    | 0.82 ± 0.00                       | 0.43 ± 0.04                            | 0.39 ± 0.01                  |                             |
| 2   | Bf      | 0.04 ± 0.01                    | 0.71 ± 0.03                       | $0.46 \pm 0.03$                        | 0.62 ± 0.00                  |                             |
| 3   | Bf1_    | 0.06 ± 0.01                    | 0.18 ± 0.00                       | <u>1.72 ± 0.04</u>                     | 0.95 ± 0.01                  |                             |
| 4   | I18m    | 0.05 ± 0.01                    | 0.22 ± 0.06                       | 1.43 ± 0.08                            | 1.09 ± 0.00                  |                             |
| 5   | Ap      | 1.78 ± 0.01                    | 7.10 ± 0.20                       | $32.4 \pm 0.0$                         | 1.84 ± 0.03                  |                             |
| 6   | 8g ·    | 0.72 ± 0.01                    | 9.52 ± 0.09                       | 34.3 ± 0.2                             | 4.31 ± 0.09                  |                             |
| 7   | Ap_     | 1.13 ± 0.05                    | 3.45 ± 0.01                       | 34.7 ± 0.0                             | 2.03 ± 0.02                  |                             |
| 8   | Bg      | 0.56 ± 0.00                    | 6.85 ± 0.21                       | $34.4 \pm 0.0$                         | 5.03 ± 0.05                  |                             |
| 9   | Ap      | 2.09 ± 0.01                    | 4.73 ± 0.04                       | 39.5 ± 0.2                             | 1.96 ± 0.04                  |                             |
| 10  | Bg      | 1.89 ± 0.01                    | 4.93 ± 0.07                       | 55.9 ± 1.5                             | 4.08 ± 0.02                  |                             |

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Figure 3.4 dQv/dpH versus pH for all soils.

the Ap and Bg horizons are similar. At least three maxima can be detected for each horizon. The maxima are located at a pH of about 4, 6 and 8. The last is less define than the others. A fourth maximum is expected at pH 10 or higher because the slope always increases at high pH. According to the hypothesis in chapter II, each of these maxima will represent one specific type of site having its own surface ionization constant and total or maximum surface charge. In the case of the podzolic soils, only one maximum can be detected with precision at around pH 4.5 and the values increased after pH This situation does not mean that there are no other types 5. of sites that contribute to the pH-dependent surface charge, but rather that there may be two or three sites with log K's close enough together so that there is no definite maximum but rather a continuous increase in the dQv/dpH.

A typical fit of the data is presented in Figure 3.5 for the Ap horizon of the Rideau soil. Observed data were fitted using the following constants;  $\log K_{(1)}=-4.14$ ,  $\log K_{(2)}=-6.44$ ,  $\log K_{(3)}=-8.13$ ,  $\log K_{(4)}=-9.76$  with the corresponding  $Qm_{(1)}=9.07$ ,  $Qm_{(2)}=4.89$ ,  $Qm_{(3)}=10.7$  and  $Qm_{(4)}=16.3$  cmol<sub>c</sub> kg<sup>-1</sup>.

The corresponding  $Qm_{(i)}$ 's for each type of site are different for each soil, and are thought to correspond to a particular soil component. A correlation matrix was calculated for the  $Qm_{(i)}$  values and the following soil properties; specific surface area, clay content, organic carbon, organic complex of Al and Fe and amorphous Al and Fe oxides. The term amorphous is defined as the difference between the  $NH_4$ -oxalate and Na-pyrophosphate extractable Al and Fe.

With the exception of  $Qm_{(1)}$  all  $Qm_{(i)}$ 's are highly correlated with the soil properties (Table 3.7). Because of the poor correlation for  $Qm_{(1)}$  the data were divided into two groups, soils with % clay lower and higher than 50 %, and new correlations and regressions calculated. For the soil horizons with less than 50 % clay, the best fit is;  $Qm_{(1)} = 0.0404 + 1.1859$  % C organic,  $R^2 = 0.923$ , n=4 [3.1a] and for the soil horizons with more than 50 % clay , the best fit is;

 $Qm_{(1)} = 5.6571 + 0.5811$  % C organic,  $R^2 = 0.603$ , n=6 [3.1b]



Figure 3.5 Observed and predicted dQv/dpH - pH plot for the Ap horizon of the Rideau soil.

| Table : | 3.7   | Correlation | coefficients | between | Qm <sub>(i)</sub> 's | and | soil |
|---------|-------|-------------|--------------|---------|----------------------|-----|------|
| propert | ties. |             |              |         |                      |     |      |

| Cm <sub>(i)</sub> | log K <sub>Ø</sub> | Soil Properties                                                                                                   | R <sup>2</sup>                            |
|-------------------|--------------------|-------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| Qm(1)             | -4.14              | specific surface area (m <sup>2</sup> g <sup>-1</sup> )<br>% clay<br>% C organic<br>% Fe amorphous                | 0.641<br>0.631<br>0.541<br>0.435          |
| Qm <sub>(2)</sub> | -6.44              | <pre>% (Fe+Al) oxalate<br/>% (Fe+Al) pyrophosphate<br/>% Fe oxalate<br/>% Al pyrophosphate<br/>% Al oxalate</pre> | 0.934<br>0.927<br>0.927<br>0.920<br>0.874 |
| Om <sub>(3)</sub> | -8.13              | % (Fe+Al) oxalate<br>% Al pyrophosphate<br>% Al oxalate<br>% (Fe+Al) amorphous<br>% Fe oxalate                    | 0.975<br>0.951<br>0.943<br>0.917<br>0.904 |
| Om <sub>(4)</sub> | -9.76              | % Fe pyrophosphate<br>% (Fe+AL) pyrophosphate<br>% Al pyrophosphate<br>% (Fe+AL) oxalate<br>% Al oxalate          | 0.987<br>0.985<br>0.955<br>0.866<br>0.702 |

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The regression equation between the  $Qm_{(2)}$  versus the (Fe+Al) oxalate is;

 $Qm_{(2)} = 0.6208 + 3.3659$  (Fe+Al) oxalate,  $R^2 = 0.934$ , n=10 [3.2]

The pyrophosphate extractable Al and Fe appeared to be well correlated with the  $Qm_{(3)}$  and  $Qm_{(4)}$  respectively. The two linear equations representing these relationships are:  $Qm_{(3)} = -0.5863 + 109.244$  % Al pyrophosphate,  $R^2=0.951$ , n=10 [3.3] and

Qm<sub>(4)</sub> = 3.8893 + 147.465 % Fe pyrophosphate, R<sup>2</sup> = 0.987, n=10 [3.4]

The  $Qm_{(3)}$  was also well correlated with oxalate extractable Al and Fe, but the regression equation in this case gives a y-intercept of -17.546, which was judged as unrealistic. Consequently a chemical components well correlated and y-intercepts close to zero were used.

#### 3.3.6 pH-dependent Surface Charge Model

The pH-dependent surface charge (Qv) of a given soil can be computed according to the following equation;

 $Qv = \Sigma Qv_{(i)}$ , for i = 1, 2, 3 and 4 [3.5] where  $Qv_{(i)}$ , in the form of the Langmuir equation, will be;

$$Qv_{(i)} = K_{(i)}Qm_{(i)}/(K_{(i)}+[H^{*}])$$
 [3.6]

while the total CEC (Qnet) at any given pH will be;

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$$Qnet = Qp + \Sigma Qv_{(i)}$$
 [3.7]

where Qp is a correction factor to adjust the pH-dependent CEC to a known value of the CEC at a given pH. By using equation 3.6 it is possible to calculate the pH-dependent contribution of the different Qv<sub>(i)</sub> to the variable charge. From this calculation (data not shown), for the podzolic soil horizons, most of the pH-dependent surface charge below pH 6.0-6.5, is controlled by the functional groups associated with the organic carbon. In the pH range 6.0 to 7.0, the type of site that contributes the most variable charge is that associated with the oxalate extractable forms of Al and Fe. At higher pH, successively organically complexed Fe and Al will control the pH-dependent surface charge. On the other hand, for the gleysolic soil horizons, between pH 3 and 8, the surface functional groups associated with the organic carbon fraction in the soil contribute the greatest arount of pH-dependent surface charge.

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It appears that at low pH (3 to 5), the soil component that will control the pH-dependent CEC is the amount of organic matter for all soils. According to this model, at pH 5, most of the sites on the organic matter will undergo deprotonation reactions. It has often been reported in the literature that the pH-dependent CEC is well correlated with the amount of organic matter and Fe and Al extractable by  $NH_4$ oxalate (Evans, 1982; Duquette and Hendershot, 1987).

In order to verify the validity of equations 3.1 to 3.4

in characterizing the pH-dependent surface charge, the values of  $Qm_{(i)}$ , log  $K_{(i)}$  and Qp were used to compute the variation of the total CEC versus the pH. The results of this computation are presented in Figure 3.6 for the Ap and Bg horizon of the gleysolic soils and Figure 3.7 for the horizons of the podzolic soils. As can be seen, the predicted values calculated from the soil properties agree fairly well with the pH-dependent surface charge measured by ion adsorption.

This implies that with a minimum knowledge of soil chemical constituents, it should be possible to predict the pH-dependent surface charge of the soil. The only problem in calculating the variation of the total CEC as a function of the pH is the determination of the correction factor (Qp) used in equation 3.7. This factor is associated with surface charge that is independent of pH. During soil formation, organic and amorphous complexes of Al and Fe form coatings on the clay particles and therefore the pH-independent CEC is not equal to the charge deficiency resulting from isomorphous substitution in the clay minerals. This factor is probably the only one that can not be calculated from soil properties, because it will depend on the mineralogy and the interactions with the coatings. Further, Qp will have different values for two soils having the same amount of clay, if one is dominated by vermiculite and the other by kaolinite, for example. DeKimpe et al. (1979) used this approach by assigning different values for Qp to different clay minerals in a soil



Figure 3.6 Total CEC measured by ion adsorption and predicted pH-dependent surface charge, adjusted to a known value of the CEC, for the gleysolic soils.

and then calculating the total CEC for the whole sample.

#### 3.3.7 Significance of the Regression Parameters

Using the regression coefficients in the linear equations relating the  $Qm_{(i)}$ 's to the soil components, it is possible to calculate the total CEC of these components. For the  $Qm_{(1)}$ , related to the \* of organic C, it is found that the CEC is 119  $\pm$  24 cmol<sub>c</sub> kg<sup>-1</sup> and 58  $\pm$  24 cmol<sub>c</sub> kg<sup>-1</sup> of organic C for the soils having less and more than 50\* of clay respectively. These values agree with those found by other scientists for the CEC of the organic C in soils (organic matter). A CEC



Figure 3.7 Total CEC measured by ion adsorption and predicted pH-dependent surface charge, adjusted to a known value of the CEC, for the podzolic soils.

between 30 and 300 cmol<sub>c</sub> kg<sup>-1</sup> is usually observed for the organic C (Hallsworth and Wilkinson, 1958; Wilding and Rutledge, 1966; McLean and Owen, 1969; Curtin and Smillie, 1976; Kalisz and Stone, 1980).

Little information in the literature is available on the total surface charge of the Al and Fe forms extractable by Napyrophosphate. However, in this study it appears that the total CEC, as calculated from the regression, is equal to  $14747 \pm 992$  and  $10924 \pm 1259 \text{ cmol}_c \text{ kg}^{-1}$  for organically complexed Al and Fe respectively. These soil components are associated with  $Qm_{(3)}$  (organic Fe) and  $Qm_{(4)}$  (organic Al). The total surface charge for  $Qm_{(2)}$  was found to be  $337 \pm 45 \text{ cmol}_c$   $kg^{-1}$ , related to the  $NH_2$ -oxalate extractable Al and Fe.

All the constants  $(K_{(i)}, Qm_{(i)})$  in this study were determined in 0.1 M Ca $(NO_3)_2$ . This implies that at the present time it is not known if they are valid for the surface charge measured in other ionic strengths or electrolyte solutions.

## 3.4 Conclusions

From this study it is concluded that the backtitration method proposed in chapter II is a useful technique to assess the pH-dependent surface charge of soils. It was assumed, in the development of the backtitration model, that the surface charge is generated only by negative surface functional groups, however if the soil possesses a significant amount of positive surface charge, the resulting backtitration method will give the net surface charge.

The measured pH-dependent CEC by backtitration is very close to that determined by ion adsorption. However, it needs a known value of the total CEC near the soil pH to adjust the pH-dependent CEC to obtain the true variation of the CEC with pH.

The backtitration technique gives a pH-dependent curve with inflection points and plateaus. The different constants derived from the inflection points and plateaus can be related to soil constituents occurring mainly as surface coatings on the soil particles. Organic matter, organic and amorphous complexes of Al and Fe seem to be the soil constituents responsible for the pH-dependent CEC of the soils used in this study. All the constants and the surface charge values derived in this study are for surface charge measured in 0.1 M  $Ca(NO_3)_2$ .

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# CONNECTING PARAGRAPH

A backtitration method was developed for soils in the preceding chapters. The main objective was to model the pHdependent surface charge of soil using a technique that is not time consuming and that corresponds to the pH-dependent surface charge measured by the ion adsorption method. This objective was fulfilled in chapter III. Chapter IV is designed to verify the application of this backtitration technique, compared to traditional potentiometric titration and ion adsorption methods, for the measurement of the pHdependent surface charge of montmorillonite, Al-oxide and chemical mixtures of both minerals. In addition, the following chapter will contained a discussion on whether the permanent charge of these chemical mixtures can be measured by the Uehara and Gillman (1980) model.

CHAPTER IV

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EFFECT OF AL OXIDE COATINGS ON THE SURFACE CHARGE BEHAVIOR OF A MONTMORILLONITE.

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# 4.0 Effect of Al Oxide Coatings on the Surface Charge Behavior of a Montmorillonite

# 4.1 Introduction

Several models have been proposed for the interpretation of the surface charge of a mixture having variable and permanent charged minerals (Uehara and Gillman, 1980; Gillman and Uehara, 1980; Madrid and Diaz-Barrientos, 1988; Madrid et al., 1989). One of these is the model of Uehara and Gillman (1980) that uses a combination of potentiometric titration and ion adsorption methods to determine the permanent charge of a mixture. This model has been criticized because (1) it is unrealistic to assume that the surface potential, calculated by the Nernst equation, is not influenced by the permanent surface charge generated by isomorphous substitution inside the clay mineral (Madrid et al., 1984), (2) the model is only applicable to a mechanical mixture of minerals as opposed to coatings of variable charge materials on permanent charge surfaces and (3) it is not possible to determine the value of the permanent charge using this model when there is no cross over point of the titration curves in different concentrations of supporting electrolyte.

Hydroxy Al interlayered (HAI) materials are commonly found in soils and efforts have been made to characterize the properties of these materials (Frink, 1965; Weismiller et al.,

1967; DeKimpe and Laverdière, 1980; Karathanasis et al., 1983; Matsue and Wada, 1988; Karathanasis, 1988). The pH-dependent charge of HAI vermiculite or partially chloritized vermiculite has been attributed to the charge arising from the deprotonation at the surface of the oxide coatings and/or the broken edges of the permanent charge minerals, while the pHindependent charge was considered as being due to the remaining charge after the blocking of the surface by the positively charged hydroxy Al (DeVilliers and Jackson, 1967). Similar observations have been reported for natural Fe oxidekaolinite complexes (Sumner, 1963; Davidtz and Sumner, 1965).

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After coating an illite clay with hydroxy Al i<sup>+</sup> was found, from electrophoretic mobility (EM) measurements, that no coatings occurred on the external surface of the clay, rather the hydroxy Al was located in the interlayer space (Harsh et al., 1988). This implies that only the nature of the saturating cations on the external surfaces will determined the magnitude and the sign of the EM. If there is any pH-dependent CEC associated with the HAI coatings, it is the result of the dissolution of the Al from the HAI or the crystal lattice of the clay mineral, and the subsequent adsorption of Al on the external surfaces (Harsh et al., 1988).

The hydroxy Al coatings on an illite decreased markedly the percentage of clay dispersed in solutions of NaCl and CaCl, (El-Swaify and Emerson, 1975). This was explained by the

increase of the surface coverage of the Al coatings on the particles. Aluminum oxide with a sheet structure is allowed to penetrate into the interlayer space. Iron oxide behaves differently because its structure is more spherical and the entry into the interlayer space is almost impossible: therefore the reduction in the percentage of clay dispersed is lower (El-Swaify and Emerson, 1975; Goldberg and Glaubig, 1987; Oades, 1984).

The adsorption of hydroxy Al polymers by montmorillonite has been reported as a cause for CEC reduction, because the hydroxy Al polymers occupied or blocked exchange sites (Kozak and Huang, 1971). Similarly, the addition of Al coatings reduced the surface charge of kaolinite and illite samples (Hendershot and Lavkulich, 1983).

CEC reduction has also been observed on smectite when adsorbed polycations of Al are present (Shen and Rich, 1962; Meyers and Ahlrichs, 1972; Keren et al., 1977; Rengasamy and Oades, 1978; Keren, 1986). However, some scientists have reported that no reduction was observed (Ragland and Coleman, 1960; Frink and Peech, 1963).

It has been observed that Al hydroxy polymers adsorbed on smectite, having an OH/Al < 2.0 and a molecular weight < 50,000, have a chain structure that is chemically sorbed on the OH<sup>-</sup> groups at the surface of the clay. The CEC reduction occurs either by the neutralization of the negative charge of these OH<sup>-</sup> groups by the polymers or by blocking of the

negative charge of the clay associated with the bridging of the clay particles and subsequent flocculation. On the other hand, large polymers, having an OH/Al > 2.0 and a molecular weight > 100,000, precipitated as gibbsite in a planar structure that can enter the interlayer space of the montmorillonite and cause CEC reduction (Rengasamy and Oades, 1978).

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The CEC reduction on hydroxy Al clay complexes has been found to be a function of the titration rate, the faster the speed of the titration, the greater the reduction. Drying the clay in the alkaline pH range increases the CEC compared to the nondried clay. On the other hand, drying the clay at pH 6 affects mainly the number of plates in an aggregate (Keren, 1980).

The adsorbed polymers of Al on a smectite sample have been found to contain 15-30 Al atoms in a planar sheet carrying a charge of 0.49+. The polymers can also increase the specific surface area (SSA), as measured by  $N_2$ , by preventing the collapse of the interlayer space (Oades, 1984). The OH/Al ratio of hydroxy Al polymers adsorbed on a montmorillonite is similar to the OH/Al ratio of the polymer in solution and only about 20 % of the adsorbed polymer is extracted with 1 N KCl (Singh and Kodama, 1988).

The purpose of this study is: 1) to verify the model of Uehara and Gillman (1980) using a chemical mixture of Al oxide precipitated onto the surface of a montmorillonite, and 2) to

measure the variation of the pH-dependent CEC following Aloxide coating.

# 4.2 Materials and Methods

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# 4.2.1 Aluminum Oxide Coatings

Aluminum oxide was precipitated onto the surface of the montmorillonite in three concentrations, 0% (mt), 50% (mt50) and 100% (mt100) of the total CEC. The procedure used to coat the montmorillonite sample is similar to that of Hendershot and Lavkulich (1983). Four hundred grams of montmorillonite was suspended in H,O in a 2 L beaker with continuous stirring. Enough 1 M AlCl, solution was then added to saturate 0, 50 and 100% of the CEC of the montmorillonite. With the help of a peristaltic pump, NaOH was slowly added to the suspension at a rate of 0.2 mmole of OH min<sup>-1</sup>, until the pH reached 7.5. The suspension was equilibrated 24 h, and then retitrated to pH This readjustment of the pH was repeated on a daily 7.5. basis for one week. The suspension was quantitatively transferred into dialysis tubing, and placed in a distilled water bath at room temperature for 12 d., replacing the water twice a day to remove the excess salt until no chloride was detected by the AgNO, test. At the end of this time the suspension was removed from the dialysis tubing and placed in a 1 L beaker and slowly heated to 60°C during 12 h following

by a successive rehydration. This treatment was repeated each day for 2 weeks. The dry sample was then crushed with a mortar and passed through a 500  $\mu$ m sieve. Pure Al oxide was prepared in the same manner without the clay.

# 4.2.2 Sample Characterization

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The exchangeable cations remaining following the coating treatment were removed by 2 h shaking with 0.1 M BaCl<sub>2</sub> (Hendershot and Duquette, 1986). The Na-pyrophosphate, NH<sub>4</sub>oxalate and citrate-bicarbonate-dithionite extractions for Al, Fe and Si were performed according to the procedure described in McKeague (1978). The total chemical composition of the samples was determined using X-ray fluorescence spectroscopy. The specific surface area of the samples was evaluated by the ethylene glycol monoethyl ether method of Eltantawy and Arnold (1973).

Infrared spectroscopy and X-ray diffraction were used for mineral identification and detection of impurities in the samples. X-ray diffraction of oriented aggregate samples was performed on the Mg, Mg-ethylene glycol, K air-dried and K heated to 300 and 550°C states according to Whittig (1965).

# 4.2.3 Surface Charge Measurements

The ion adsorption, potentiometric titration and

backtitration procedures used to characterize the surface charge of the samples were the same as described in Chapter III. However the electrolyte concentrations were 0.005 M  $Ca(NO_3)_2$  for the ion adsorption method, and 0.0005, 0.005 and 0.05 M  $Ca(NO_3)_2$  for the potentiometric titrations. pHdependent CEC by ion adsorption was performed on a reduced charge montmorillonite obtained by washing the clay sample five times with 1 M of LiCl (Greene-Kelly, 1955; Jaynes and Bigham, 1987). The clay sample was then oven-dried at 110°C and heated at 250°C for 12 h in a silica crucible (Lim and Jackson, 1986) prior to CEC measurements.

# 4.2.4 Physical Properties

Two additional physical properties measured on the clay samples were the optical density (OD) and the sedimentation volume (SV). The sedimentation volume was measured in calibrated cylinders by adding 80 to 90 mg of Ca-saturated clay to 25 mL of 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> adjusted to a range of pH values between 3 and 8. The thickness of the clay suspension at the bottom of the cylinders was evaluated at 24 and 48 h. Because the two measurements were the same, only the 24 h values are reported.

The OD of the Ca-saturated clay suspensions (0.02-0.04% w/v), at three different pH values, was measured in the 200-800 nm wavelength range using a spectrophotometer with

distilled deionized water as the reference. The path length was 1 cm and the OD values can be directly converted to the absorbance index "K" values. The "K" values at 700 nm were used to calculate the relative number of plates per tactoid, using Banin and Lahav's equation (1968):

 $(n_i^3[n_j(d_c+1)-1]^2)/(n_i^3[n_i(d_c+1)-1]^2) = K_i/K_j$  [4.1] where,  $d_c$  is specific density of the clay (2.80 g cm<sup>-3</sup>),  $K_i$  is the absorbance indexes of the Ca-montmorillonite,  $K_j$  is the absorbance index of the Li-clay,  $n_i$  is the number of plates per tactoid of Ca-montmorillonite and  $n_j$  is the number of plates per tactoid of Li-montmorillonite. In this experiment, Li-montmorillonite was used as the reference clay, because ideal dispersion is assumed, n = 1 (Ben-Dor and Singer, 1987). The particle lengths were determined from the absorption curve in a wavelength range of 350-700 nm to calculate the linear slope "b" of the absorption curve in a log lambda-log K scale. Where b = dlog K/ dlog $\lambda$ . The major particle dimension ( $\beta$ ) was calculated as  $\beta = 4$ -b (Dufey and Banin, 1979).

4.3 Results and Discussion

4.3.1 Chemical and Mineralogical Characterization

# 4.3.1.1 Mineralogical Characterization

X-ray diffraction patterns for the mt sample are showed

in Appendix II. This sample is dominated by montmorillonite with cristobalite impurities that give a peak at about 0.41 Cristobalite is often found as an associated mineral in nm. bentonite deposits (Schultz, 1969; Henderson et al., 1971). The X-ray diffraction patterns for the mt50 and mt100 and the synthetic Al oxide are given in Appendices III, IV, and V respectively. From these X-rays patterns it is apparent that the hydroxy Al polymer coatings have no effect of blocking the collapse of the interlayer space of the mt50 sample. The mt100 sample behaves more like hydroxy interlayered smectite, showing resistance to collapse when saturated with K\* and heated to 300°C giving a peak at about 1.25 nm. However, for the Mg treated sample small differences are found in the positions of the d(001) peaks at 1.63, 1.61 and 1.58 nm for mt, mt50 and mt100 respectively (Appendices II, III, and IV). In Appendix V, two x-ray patterns are presented: the synthetic Al oxide appears to be semi-amorphous to X-rays, having very broad peaks at 0.656, 0.489, 0.438, 0.322, 0.235 and 0.186 nm; the other trace appearing represents the same sample after treatment for 1 hour in a 0.64 M solution of HNO, to remove acid soluble materials. After this treatment, a major peak is obtained at about 0.489 nm, that correspond to the d(002) of gibbsite. According to the results obtained here, it can be deduced that the synthetic Al oxide possesses a gibbsite nucleus with a surrounding amorphous layer. Because the same procedure was used to precipitate the Al oxide onto

the surface of the montmorillonite and the synthetic Al oxide, it is assumed that the Al oxide precipitates will have the same structure.

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To verify the nature of the montmorillonite sample, the Greene-Kelly test was performed. In Appendix VI the result of the X-ray diffraction pattern on this sample can be seen. As expected after Li saturation and heating, the d(001) of the sample gives a peak at 0.96 nm that does not expand upon glycerol solvation. This permanent collapsing after Lifixation has been attributed to smectite having more than 50% of the charge arising from the isomorphous substitution in the octahedral layer (Greene-Kelly, 1955).

Appendix VII and VIII present respectively the infrared trace of the samples used in this study in the range 3000-4000 cm<sup>-1</sup> and 400-1300 cm<sup>-1</sup>. It can be seen that little difference is obtained between the montmorillonite samples. The infrared trace of the Li-fixed montmorillonite shows the disappearance of the 914 cm<sup>-1</sup> absorption band leaving only a shoulder in the trace. This absorption band is attributed to the OH associated with the AlAl pair, which has been reported to decrease markedly when Li fixation occurs (Clavet and Prost, 1971). The appearance of an absorption band at 417 cm<sup>-1</sup> corresponds also to the IR spectrum for other Li-bearing smectites (Ianovici et al., 1990).

4.3.1.2 Chemical Characterization

Table 4.1 presents the results of the total chemical analysis of the samples. The high amount of  $SiO_2$  is due to cristobalite impurities in the samples. The synthetic Al oxide is almost free of impurities (< 2%) and is constituted almost exclusively of Al oxide.

To verify the amount of hydroxy Al polymers precipitated onto the surface of the mt50 and mt100, the increase of the amount of Al was calculated from the Al increase in the cxalate, CBD extraction and total chemical analysis. Table 4.2 shows the results of these measurements. As reported in this table, the difference in the amount of Al in the sample as Al, $O_3$ , between the mt50 and mt is 0.71, 0.75 and 0.64 respectively for the total chemical analysis, and the oxalate and CBD extractions. When these values are reported in cmol kg<sup>-1</sup>, they give an average of 38.9  $\pm$  3.3 cmol, kg<sup>-1</sup> (42.3 % of the CEC) of Al precipitated onto the surface. The difference in the mt100 and at samples was found to be 1.61, 1.72 and 1.30 % Al<sub>2</sub>O<sub>3</sub> precipitated. These values for the mt100 sample, represent 85.8  $\pm$  12.1 cmol kg<sup>-1</sup> (91.0 % of the CEC) of Al precipitated onto the surface. The average percentages, 42.3 % and 91.0 %, are not far from the initial target values of 50 % and 100 %.

In the oxalate and CBD extractions, Fe and Si were also analysed. It was found that the amount of extractable Fe does

not change with the increase in Al saturation. On the other hand the amount of Si extracted by oxalate seems to increase with increasing Al saturation, but remains constant in the CBD extraction.

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To verify the status of the exchangeable cations after the Al coating procedure, the exchangeable cations were measured. The sum of the exchangeable cations was 85.6, 74.4, 73.7 and 0.13  $\text{cmol}_c \text{ kg}^{-1}$  respectively for the m<sup>+</sup>, mt50, mt100 and the synthetic Al oxide samples.

The specific surface areas as measured by the ethylene glycol monoethyl ether method was  $597 \pm 4 \text{ m}^2 \text{ g}^{-1}$  for the mt sample,  $635 \pm 12 \text{ m}^2 \text{ g}^{-1}$  for the mt50 sample,  $603 \pm 13 \text{ m}^2 \text{ g}^{-1}$  for the mt100 sample and  $408 \pm 9 \text{ m}^2 \text{ g}^{-1}$  for the synthetic Al oxide sample. The Al saturation does not significantly increase the specific surface area of the montmorillonite samples.

4.3.2 Theoretical Calculation of the Permanent Charge.

Using the total chemical analysis, the chemical formulae for the montmorillonite samples are calculated with the following assumptions: (1)  $\text{TiO}_2$  and  $P_2O_5$  do not occur in the clay, (2) an ideal framework of  $O_{20}(OH)_4$  is used, (3) the total concentration of Mg in the octahedral layer is corrected for exchangeable Mg<sup>2+</sup>, (4) the charge deficit of the octahedral

| 1 | Table 4.1            | Total chemi | cal analysis |        |
|---|----------------------|-------------|--------------|--------|
|   | Element              | Mt          | Mt-50        | Ht-100 |
|   | sio <sub>z</sub> (%) | 61.6        | 61.1         | 60.3   |

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| sio <sub>2</sub> (%)                 | 61.6 | 61.1 | 60.3 | 0.81   |
|--------------------------------------|------|------|------|--------|
| TiO <sub>2</sub> (%)                 | 0.24 | 0.22 | 0.23 | 0.01   |
| Al <sub>2</sub> 0 <sub>3</sub> (%)   | 15.6 | 16.3 | 17.2 | 64.4   |
| Fe <sub>2</sub> C <sub>3</sub> (%)   | 1.03 | 0.81 | 0.83 | 0.08   |
| Mn0 (%)                              | 0.03 | 0.02 | 0.02 | 0.01   |
| Mg0 (%)                              | 3.14 | 3.09 | 2.97 | 0.06   |
| CaO (%)                              | 1.88 | 1.68 | 1.48 | 0.02   |
| Na <sub>2</sub> 0 (%)                | 1.01 | 0.17 | 0.36 | < 0.01 |
| K <sub>2</sub> 0 (%)                 | 0.12 | 0.04 | 0.05 | 0.02   |
| P <sub>2</sub> 0 <sub>5</sub> (%)    | 1.37 | 1.08 | 1.23 | < 0.01 |
| LOI (%)                              | 14.6 | 16.2 | 16.1 | 33.7   |
| V (ppm)                              | < 10 | < 10 | < 10 | < 10   |
| Cr <sub>2</sub> 0 <sub>3</sub> (ppm) | 23   | < 15 | < 15 | < 15   |
| Ni (ppm)                             | 38   | < 10 | < 10 | < 10   |
| BaO (ppm)                            | 119  | 66   | 132  | 19     |

Al-oxide

|                                        |                                   | NH₄ - Oxal                            | ate                                |             |            |  |
|----------------------------------------|-----------------------------------|---------------------------------------|------------------------------------|-------------|------------|--|
| San                                    | ple                               | AL (%)                                | Fe (%)                             | Si (%)      |            |  |
| Mt                                     |                                   | 0.19 ± 0.01                           | 0.02 ± 0.00                        | 0.07 ± 0.03 |            |  |
| Mt50                                   |                                   | 0.59 ± 0.01                           | 0.02 ± 0.00                        | 0.12 ± 0.02 |            |  |
| Mt100                                  |                                   | 1.10 ± 0.03                           | 0.02 ± 0.00                        | 0.26 ± 0.13 |            |  |
|                                        | Ci                                | trate - Bicarbonat                    | e - Dithionite                     |             |            |  |
| Sam                                    | ple                               | AL (%)                                | Fe (%)                             | Si (%)      |            |  |
| Mt                                     |                                   | 0.08 ± 0.01                           | 0.04 ± 0.01                        | 0.14 ± 0.02 |            |  |
| Mt50                                   |                                   | 0.42 ± 0.01                           | 0.03 ± 0.00                        | 0.13 ± 0.01 |            |  |
| Mt100                                  |                                   | 0.77 ± 0.01                           | 0.03 ± 0.00                        | 0.13 ± 0.01 |            |  |
| <u> </u>                               |                                   | % Al <sub>2</sub> 0 <sub>3</sub> Satu | ration                             |             | <u> </u>   |  |
| Sample                                 | Nt                                | Nt50                                  | Ht100                              | Mt50 - Mt   | Mt100 - Mt |  |
| % Al <sub>2</sub> O <sub>3</sub> total | 15.6                              | 16.3                                  | 17.2                               | 0.71        | 1.61       |  |
| % Al <sub>2</sub> O3 oxalate           | 0.36                              | 1.11                                  | 2.08                               | 0.75        | 1.72       |  |
| X AL <sub>2</sub> O3 CBD               | 0.15                              | 0.79                                  | 1.45                               | 0.64        | 1.30       |  |
| CEC saturation                         |                                   |                                       |                                    |             |            |  |
| Sample                                 | Mt50                              | - Ht                                  | Ht100 - Ht                         |             |            |  |
| •                                      | cmol <sub>c</sub> kg <sup>1</sup> | X CEC <sup>(1)</sup>                  | cmol <sub>c</sub> kg <sup>-1</sup> | X CEC       |            |  |
| Al total                               | 39.5                              | 41.9                                  | 89.5                               | 94.9        |            |  |
| Al oxalate                             | 41.7                              | 44.2                                  | 95.6                               | 101         | L          |  |
| AL CBD                                 | 35.6                              | 37.7                                  | 72.3                               | 76.6        |            |  |

# Table 4.2 NH,-oxalate, CBD extraction and Al saturation data

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layer is assumed to be the difference between the CEC of Casaturated and Li-fixed montmorillonite (delta=78.3 cmol<sub>c</sub> kg<sup>-1</sup>) (Jaynes and Bigham, 1987) and (5) cristobalite (SiO<sub>2</sub>) has no CEC but has a dilution effect in the sample. From the total chemical composition, the chemical formula is calculated by varying the amount of SiO<sub>2</sub> attributed to cristobalite until the octahedral layer charge, once corrected for the dilution, gives a CEC of about 78 cmol<sub>c</sub> kg<sup>-1</sup>. The amount of SiO<sub>2</sub> as cristobalite is found to be 15 %. The resulting chemical formula per unit cell is:

 $X_{0.78}(Si_{7.90}Al_{0.10})(Al_{3.128}Fe_{0.136}Mg_{0.759})O_{20}(OH)_{4}$  [4.2]

The total layer charge is 0.780, with 0.100 and 0.680 arising from the tetrahedral and octahedral layers respectively. Once the dilution effect of the 15% of cristobalite is taken into account, this gives a total CEC of 89.7  $\text{cmol}_c$  kg<sup>-1</sup> with 11.5 and 78.3  $\text{cmol}_c$  kg<sup>-1</sup> arising from the tetrahedral and octahedral layers respectively, caused by isomorphous substitution in these layers.

The crystallographic surface area calculated from chemical composition (Gast, 1977) is 768 m<sup>2</sup> g<sup>-1</sup> for the montmorillonite alone and 640 m<sup>2</sup> g<sup>-1</sup> for the sample, assuming a specific surface area of 0 m<sup>2</sup> g<sup>-1</sup> for the cristobalite. The specific surface area of  $SiO_2$  minerals, opal excluded, is usually < 4 m<sup>2</sup> g<sup>-1</sup> (Wilding et al., 1977). The calculated crystallographic surface area is close to that measured by the ethylene glycol monoethyl ether method of 597 ± 4 m<sup>2</sup> g<sup>-1</sup>.

The chemical formula based on a half unit cell is;

 $X_{0.390}(Si_{3.95}Al_{0.05})(Al_{1.564}Fe_{0.068}Mg_{0.380})O_{10}(OH)_{2} [4.3]$ According to Sposito (1986), montmorillonite formation can be visualized as the polymerization of the different hydroxide components by the following reaction;  $nC(OH)_{z}(s) + n_{1}Si(OH)_{4}(s) + n_{2}Al(OH)_{3}(s) + n_{3}Fe(OH)_{3}(s) +$  $n_{4}(Mg(OH)_{2}(s) \leftarrow C_{n}Si_{n1}Al_{n2}Fe_{n3}Mg_{n4}O_{10}(OH)_{2}(s) + (x + \Sigma n_{i}z_{i} 12)H_{2}O(1)$  [4.4]

Where C is the exchangeable cation and x the layer charge. The standard Gibbs energy change for this reaction is:

$$\Delta G_{r}^{\circ} = \mu^{\circ}_{\text{montmorillonite}} + (x + \Sigma n_{i}z_{i} - 12)H_{2}O(1) - n\mu^{\circ}_{C(OH)z(s)} -\Sigma n_{i}\mu^{\circ}_{i} \qquad [4.5]$$

and the chemical standard potential of montmorillonite is defined as:

$$\mu^{\circ}_{mt} = n\mu^{\circ}_{C(OR)z(s)} + \Sigma n_{i}\mu^{\circ}_{i} - (x + \Sigma n_{i}z_{i} - 12)H_{2}O(1) - |\Delta G_{r}^{*}|$$
[4.6]

where,  $|\Delta G_r^*|$  can be computed by a linear equation, knowing: (1) the layer charge "x", (2) the Shannon-Prewitt radius "Ri" and (3) the valence "z" of the exchangeable cation. Consequently,

$$|\Delta G_r| = 41.34 + 921.66(xRi/z)$$
 [4.7]

Equation 4.7 was developed by Mattigod and Sposito (1978) for 25 montmorillonites, and it was assumed to be applicable in this study. From this calculation, the value of the standard chemical potential for the Ca-saturated montmorillonite is,  $\mu_{Ca-mt}^{*} = -5316$  kJ mol<sup>-1</sup>. This is in agreement with the standard chemical potential obtained for montmorillonites (Sposito, 1986).

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Using this value, the solubility constant for the Casaturated montmorillonite (log  $K_{so}$ ) has been calculated to be equal to 3.67 for the following reaction;

$$Ca_{0.169}(Si_{3.95}Al_{0.05})(Al_{1.564}Fe_{0.068}Mg_{0.380})O_{10}(OH)_{2}(S) +$$

$$3.80H_{2}O(1) + 6.20H^{*}(aq) \Rightarrow 0.169Ca^{2*} + 3.95H_{4}SiO_{4}^{*} +$$

$$1.614Al^{3*} + 0.068Fe^{3*} + 0.380Mg^{2*} \qquad [4.8]$$

Rearranging this equation to obtain a coefficient of unity for pH-0.33pAl gives;

The determination of the chemical formula of the hydroxy precipitated onto Al polymer the surface of the montmorillonite was done following the procedure of Hsu and Bates (1964). Some reduction of the surface charge occurred in the sample upon Al saturation/precipitation. This reduction was measured in two ways: from the amount of exchangeable cations extracted in 0.1 M BaCl,, and from the total CEC measured in 0.005 M Ca(NO<sub>3</sub>), without adjusting the pH with acid or base. The results of this calculation are presented in Table 4.3. The average OH/Al ratio of the precipitated Al polymers is 2.13  $\pm$  0.07 and 2.57  $\pm$  0.06 for the mt50 and mt100 respectively.

| Sample                                              | Oxalate                                                      | CBD                    | Total                                     |                              |  |
|-----------------------------------------------------|--------------------------------------------------------------|------------------------|-------------------------------------------|------------------------------|--|
|                                                     | charge reduction                                             |                        |                                           |                              |  |
| Mt-50                                               | 3.75                                                         | 3.20                   | 3.55                                      | 0.113                        |  |
| Mt-100                                              | 8.60                                                         | 6.50                   | 8.05                                      | 0.120                        |  |
| mg of Al fixed / meq of exchange charge inactivated |                                                              |                        |                                           | mean ±<br>standard deviation |  |
| Mt-50                                               | 33.2                                                         | 28.3                   | 31.4                                      | 31.0 ± 2.5                   |  |
| Mt-100                                              | 71.9                                                         | 54.4                   | 67.3                                      | 64.5 ± 9.1                   |  |
| n                                                   | mber of positive charg                                       | ge on the OH-Al polyme | ers                                       | mean ±<br>standard deviation |  |
| Mt-50                                               | 0.81+                                                        | 0_95+                  | 0.86+                                     | 0.87 ± 0.07+                 |  |
| Mt-100                                              | 0.38+                                                        | 0.50+                  | 0.40+                                     | 0.43 ± 0.06+                 |  |
|                                                     | OK/Al ratio of the polymers precipitated                     |                        |                                           |                              |  |
| Mt-50                                               | 2.19                                                         | 2.05                   | 2.14                                      | 2.13 ± 0.07                  |  |
| Mt-100                                              | 2.62                                                         | 2.50                   | 2.60                                      | 2.57 ± 0.06                  |  |
| numbers of Al atoms per unit cell                   |                                                              |                        |                                           | mean ±<br>standard deviation |  |
| Mt-50                                               | 0.130                                                        | 0.111                  | 0.123                                     | 0.121 ± 0.010                |  |
| Mt-100                                              | 0.295                                                        | 0.223                  | 0.276                                     | 0.265 ± 0.037                |  |
|                                                     | Chemica                                                      | l formula of the Al p  | olymers                                   |                              |  |
| Methods                                             | Mt-50 Mt                                                     |                        |                                           | -100                         |  |
| Oxalate extraction                                  | Al <sub>0.130</sub> (OH) <sub>0.285</sub>                    |                        | AL <sub>0.295</sub> (OH) <sub>0.773</sub> |                              |  |
| CBD extraction                                      | AL <sub>0.111</sub> (OH) <sub>0.228</sub>                    |                        | Al <sub>0.223</sub> (OH) <sub>0.558</sub> |                              |  |
| Total analysis                                      | Al <sub>0.123</sub> (OH) <sub>0.263</sub> Al <sub>0.27</sub> |                        | (OH) <sub>0.718</sub>                     |                              |  |
| Average chemical formula of the Al+OH polymers      |                                                              |                        |                                           |                              |  |
| Mt-50                                               | AL <sub>0.121</sub> (OH) <sub>D.250</sub> 0.104+             |                        |                                           |                              |  |
| Mt-100                                              | AL <sub>0.265</sub> (OH) <sub>0.663</sub> 0.112+             |                        |                                           |                              |  |
|                                                     |                                                              |                        |                                           |                              |  |

Table 4.3 Chemical formula of the precipitated Al polymers

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Based on one mole of Al, the average chemical composition of the Al polymers for mt50 and mt100 are respectively  $Al(OH)_{2.13}^{0.87+}$  and  $Al(OH)_{2.57}^{0.43+}$ . When these formulae are corrected for the number of atoms of Al per unit cell (montmotillonite), as described by Kirkland and Hajek (1972), they give average chemical formulae of:

$$Al_{0.121}(OH)_{0.259}^{0.104+}$$
 for Mt50;  
and

1.0

$$Al_{0.265}(OH)_{0.683}^{0.112+}$$
 for Mt100.

Based on these formulae, and assuming no change in the chemical formula of the montmorillonite, the chemical formulae of the hydroxy Al interlayered montmorillonites are:

#### Mt-50

$$X_{0.676}(Si_{7.90}Al_{0.10})(Al_{3.128}Fe_{0.136}Mg_{0.759})[Al_{0.121}(OH)_{0.259}]O_{20}(OH)_{4}$$
 [4.10]  
Mt-100

 $X_{0.668}(Si_{7.90}Al_{0.10})(Al_{3.128}Fe_{0.136}Mg_{0.759})[Al_{0.265}(OH)_{0.683}]O_{20}(OH)_{4}$  [4.11]

Using the same method of calculation for the montmorillonite, the chemical standard potentials for the hydroxy Al interlayered montmorillonites have been calculated as -5360 and -5442 kJ mol<sup>-1</sup> for the mt50 and mt100 respectively. These values are in the range of naturally occurring hydroxy Al interlayered smectites, -5933  $\pm$  610 kJ mol<sup>-1</sup> (Karathanasis, 1988). The constant of solubility (log  $K_{so}$ ) has been calculated as 4.00 and 4.43 for the Mt50 and Mt100.

### 4.3.3 Surface Charge Measurements

## 4.3.3.1 Ion Adsorption

Figure 4.1 presents the results of the total CEC and AEC versus pH for the mt, mt50, mt100 and the synthetic Al oxide. The CEC of the uncoated montmorillonite sample decreases below pH 6 from about 90 cmol<sub>c</sub> kg<sup>-1</sup> to 73 cmol<sub>c</sub> kg<sup>-1</sup> at pH 3. The increase of hydroxy Al polymers increased the CEC in both cases. This is surprising because the CEC of mt50 and mt100, from the summation of the cations displaced by neutral BaCl<sub>2</sub>, are lower than the mt sample when no acid or base are added.

The contribution of Al to the CEC increases with decreasing pH and with increasing amounts of hydroxy Al polymer precipitated onto the surface. In these cases, part of the pH-dependent CEC of hydroxy Al coated clay, is due to the adsorbed Al and to the dissolution of Al coatings. Table 4.4 presents the data for the Al status in the ion adsorption experiment. It can be seen that below pH 5.0, Al begins to dissolve, and in all cases the amount of adsorbed Al and dissolved Al increases with the increase of hydroxy Al polymer coatings. The amount of monomeric Al (Alm) dissolved is higher than that of polymeric (Alp) for the mt sample. Upon polymer coating, the ratio Alm/Alp increased. From this it can be deduced that the Alm in solution increased



Figure 4.1 CEC and AEC measured by ion adsorption for the mt, mt50, mt100 and the synthetic Al-oxide.

at low pH when the amount of coatings increased.

Figure 4.2 shows the amount of Si and Mg dissolved from the mt, mt50 and mt100 samples as a function of pH. The coating has the effect of reducing the amount of Mg and Si released into solution. However, at low pH the release of Si is the same with and without polymer coatings. The dissolution of the coatings (Table 4.4) at these pH values is responsible for this behavior.

To assess the effect of the reduction of the layer charge, the total CEC versus pH was measured on a Li-fixed montmorillonite (Li-mt) and compared with the CEC of the untreated montmorillonite (mt) (Figure 4.3). The reduction in

|        | pH Aladsorbed Almonomeric dissolved Alpolymeric d |                        |                        |  |  |  |  |
|--------|---------------------------------------------------|------------------------|------------------------|--|--|--|--|
|        | mmole kg <sup>-1</sup>                            | mmole kg <sup>*1</sup> | mmole kg <sup>-1</sup> |  |  |  |  |
|        | Kt                                                |                        |                        |  |  |  |  |
| 3.02   | 12.5                                              | 16.6                   | 21.2                   |  |  |  |  |
| 3.24   | 13.2                                              | 15.5                   | 6.87                   |  |  |  |  |
| 5.02   | 1_50                                              | 3,10                   | 9.88                   |  |  |  |  |
| 6.18   | 0.83                                              | 0.49                   | 0.73                   |  |  |  |  |
| 6.22   | 0.87                                              | 0.76                   | 0.51                   |  |  |  |  |
| 6.85   | 0.00                                              | 0.00                   |                        |  |  |  |  |
| 7 15   | 0.00                                              | 0.23                   | 0.00                   |  |  |  |  |
| 7.33   | 0.00                                              | 0.00                   | 0.00                   |  |  |  |  |
| 7.86   | 0.00                                              | 0.00                   | 0.00                   |  |  |  |  |
| 7.99   | 0.00                                              | 0.00                   | 0.00                   |  |  |  |  |
|        | Mt-50                                             |                        |                        |  |  |  |  |
| 3.27   | 76.0                                              | 49.1                   | 17.1                   |  |  |  |  |
| 3.19   | 70.4                                              | 62.3                   | 18.1                   |  |  |  |  |
| 4.31   | 0.37                                              | 2.58                   | 1 78                   |  |  |  |  |
| 5.37   | 0.00                                              | 0.06                   | 0.05                   |  |  |  |  |
| 5.48   | 0.00                                              | 0.06                   | 0.05                   |  |  |  |  |
| 6.32   | 0.00                                              | 0.00                   | 0.00                   |  |  |  |  |
| 6.34   | 0.00                                              | 0.00                   | 0.00                   |  |  |  |  |
| 6.84   | 0.00                                              | 0.00                   |                        |  |  |  |  |
| 7.51   | 0.07                                              | 0.00                   | 0.00                   |  |  |  |  |
| 7.65   | 0.00                                              | 0.00                   | 0.00                   |  |  |  |  |
| Mt-100 |                                                   |                        |                        |  |  |  |  |
| 3.39   | 129                                               | 90.9                   | 10.1                   |  |  |  |  |
| 3.43   | 120                                               | 69.2                   | 14.5                   |  |  |  |  |
| 4.27   | 24.2                                              | 12.3                   | 3.20                   |  |  |  |  |
| 4.44   | 24.1                                              | 5.71                   | 1.06                   |  |  |  |  |
| 5.51   | 0.17                                              | 0.05                   | 0.17                   |  |  |  |  |
| 6.24   | 0.00                                              | 0.00                   | 0.00                   |  |  |  |  |
| 6.28   | 0.00                                              | 0.00                   | . 0.00                 |  |  |  |  |
| 6.81   | 0.03                                              | 0.00                   | 0.03                   |  |  |  |  |
| 6.74   | 0.00                                              | 0.00                   | 0.00                   |  |  |  |  |
| 7.37   | 0.10                                              | 0.02                   | 0.15                   |  |  |  |  |
| 1.34   | 0.05                                              | 0.03                   | U.11                   |  |  |  |  |

Table 4.4 Aluminum status during the pH-dependent ion adsorption experiment

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the CEC of the Li-mt seems to be constant whatever the pH. The reduction is about 80  $\text{cmol}_c \text{ kg}^{-1}$  and the maximum CEC obtained is about 11  $\text{cmol}_c \text{ kg}^{-1}$ ; a value close to the amount of isomorphous substitution in the tetrahedral layer (11.5  $\text{cmol}_c \text{ kg}^{-1}$ ). On Li fixation a constant AEC of 0.25  $\text{cmol}_c \text{ kg}^{-1}$ 



Figure 4.2 Silica and Mg dissolved during the 24 h. equilibrium period, ion adsorption.

developed. Because of this and the constant reduction of CEC, the point of zero net charge (PZNC) for the Li-mt was calculated as equal to 3.52.

The release of Si and Mg from the Li-mt is presented in Figure 4.4. The pH-dependent release of Si is reduced upon Li fixation, but Mg seems to be released in higher amounts when there is Li in the octahedral layer.

The mt sample seems to have some pH-dependent CEC between pH 3 and 6 which corresponds roughly to the charge deficit in the tetrahedral layer. The measured pH-dependent CEC on montmorillonite can be due to three factors, (1) edge-to-face association at low pH neutralizing some of the charge, (2) pH



Figure 4.3 CEC measured by ion adsorption on the Li-fixed montmorillonite and the untreated montmorillonite.

dependent charge generated by the silanol and aluminol groups at the edges of the clay, and (3) dissolution of the crystal lattice releasing ions (mainly Al) into solution that can be subsequently adsorbed on the exchange sites.

In a Ca-montmorillonite system, face-to-face association is the dominant mode of aggregate formation and we would not expect there to be any edge-to-edge or edge-to-face association (Shomer and Mingelgrin, 1978; Dufey and Banin, 1979; Rand et al., 1980; Ben-Dor and Singer, 1987). The other explanations of the apparent pH-dependent CEC (dissolution or edge charge) are difficult to distinguish between.



Figure 4.4 Silica and Mg dissolved in the 24 h. equilibrium period by ion adsorption for the montmorillonite untreated and Li-fixed.

# 4.3.3.2 Potentiometric Titrations

The results of traditional potentiometric titrations on the mt, mt50 and mt100 are presented in Figure 4.5. No PZSE defined as the intersection of titration curves in different electrolyte concentrations was detected on these graphs. When hydroxy Al polymers are present on the surface, they change the shape of the curves but no cross over points of the titration curves in different electrolyte concentrations are detected. According to the procedure of Gillman and Uehara (1980) and Uehara and Gillman (1980), it is possible to calculate the permanent charge of the solid by ion adsorption at the PZSE of a solid. Results showed that no permanent charge could be detected for these chemical mixtures. It is surprising that this model does not work with a chemical mixture having about 80 cmol, kg<sup>-1</sup> and 11 cmol, kg<sup>-1</sup> of permanent charge arising from isomorphous substitution in the octahedral and tetrahedral layer respectively and about 50 cmol, kg<sup>-1</sup> of variable charge. Consequently, this model cannot be applied in a chemical mixture of montmorillonite and Al It is doubtful if the method of Gillman and Uehara oxide. (1980) would be able to detect small amounts of permanent charge in soils when it did not give satisfactory results in this experiment. The titration of the mt sample alone shows a surface consumption of H<sup>+</sup> of about 45 cmol, kg<sup>-1</sup> between the zero point of titration (ZPT) (ZPT = 7.13 in 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub>) and pH 3. The high consumption of H cannot be attributed to the pH-dependent surface charge determined by ion adsorption (about 17  $\text{cmol}_{c}$  kg<sup>-1</sup>) rather H<sup>+</sup> contributes to dissolution reactions.

The potentiometric titrations on the synthetic Al-oxide are presented in Appendix IX. The zero point of salt effect (PZSE) has been determined at pH = 8.75 in  $Ca(NO_3)_2$  and 9.24 in NaCl (not shown) by the cross over point of the titration curves in 0.001 and 0.01 M. These two concentrations were chosen because the titration curve in 0.1 M NaCl does not intercept the other titration curves. Because of the

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Figure 4.5 Potentiometric titrations on the mt, mt50 and mt100 samples.

solubility behavior of the synthetic Al oxide, and the subsequent effect on  $H^*/OH^-$  consumption, no attempt was made to calculate the intrinsic equilibrium constant. As mentioned by Schulthess and Sparks (1986) when only the ZPC is required, no correction for the solubility of the solid and the electrolyte concentration is required, because at the ZPC (or PZSE) the solubility and the electrolyte effects are at a minimum.

# 4.3.3.3 Backtitrations

As described in chapters II and III, a backtitration

technique similar to that of Schulthess and Sparks (1986) was developed to measure the pH-dependent CEC. To verify the validity of this technique it was applied to the mt, mt50, mt100 and the synthetic Al oxide samples. Figure 4.6 presents the results of the backtitration for the mt, mt50 and mt100 samples, conjointly with the CEC measured by ion adsorption. The backtitration curves, as mentioned in the preceding chapter, have been adjusted to a known value of the total CEC, near the sample pH. This pH corresponds approximately to the ZPT of the sample in a given electrolyte concentration. The respective ZPT's for the mt, mt50, mt100 are 7.13, 6.51 and 6.40 in 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub>.

The values used to adjust the backtitration curves to the data obtained by ion adsorption are 77.4, 79.7 and 90.5 cmol<sub>c</sub> kg<sup>-1</sup> for mt, mt50 and mt100. On Figure 4.6 it can be seen that the backtitration curves correspond to the pH-dependent CEC as measured by ion adsorption. However, at low pH for mt50 and mt100, some divergence occurs. The adsorbed Al, extracted by 1 M KCl, was measured as monomeric in solution; polymeric Al was absent. If the form of Al (Alp or Alm) is not the same in solution as on the exchange sites, it is possible that some of the Al, measured as monomeric in solution, was in fact in polymeric form when adsorbed. It has been reported earlier that the adsorbed Al can have a charge less than 3 (Bache, 1970), implying some adsorbed Alp or hydrolysis product of Al, and because the surface acidity of



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Figure 4.6 CEC measured by ion adsorption and surface charge measured by the backtitration technique for the mt, mt50 and mt100 samples.

smectite is usually 2 to 4 pH unit lower than the equilibrium pH (Bailey et al., 1968) the speciation of Al could be different at the surface than in the equilibrium solution.

In Figure 4.7, the backtitration curve for the synthetic Al oxide is presented with the  $NO_3$  adsorption in 0.005 M  $Ca(NO_3)_2$ . Again, the surface charge measured by the backtitration represents the pH-dependent net surface charge of this sample. The backtitration curve was adjusted to the PZSE determined by potentiometric titrations; surface charge = 0 at pH = 8.75. In the case of the synthetic Al-oxide, the reactions assumed to take place at the surface are:

$$= AlOH_2^+ \Rightarrow = AlOH + H^+ \qquad [4.12]$$

and

$$\equiv AlOH \Leftrightarrow \equiv AlO' + H^{*} \qquad [4.13]$$

Below the PZSE, reaction 4.12 will dominate and above the PZSE, reaction 4.13 will dominate. In chapters II and III it was assumed that only a surface reaction similar to equation 4.13 occurs. This was justified for soils from a temperate area where AEC is low and equation 4.12 could be ignored when calculating OH<sup>-</sup> consumption during backtitration. However, when the solid backtitrated possesses significant amounts of positive and negative charge, the resulting backtitration curve will represent the pH-dependent net surface charge.

## 4.3.4 Physical properties

# 4.3.4.1 Sedimentation Volume

The results of the SV experiment in 0.005 M  $Ca(NO_3)_2$  are presented in Appendix X. With the exception of the mt sample which showed an increase in the SV with an increase in pH, the SV of the mt50 and mt100 samples did not seem to be affected by pH. It was expected that the Ca saturated montmorillonite (Ca-mt) sample would have more repulsion at high pH, as demonstrated by the pH-dependent CEC, due to increased negative surface charge. However, the mt50 and mt100 had CEC that was higher than the mt sample. This can be explained by the effect of Al saturation/precipitation that not only



Figure 4.7 AEC measured by ion adsorption and surface charge measured by the backtitration technique for the synthetic Al-oxide.

blocked surface charge, but also linked clay particles together to form aggregates of higher dimension.

# 4.3.4.2 Optical Density

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Optical absorption spectra of clay minerals are useful for a semi-quantitative method of determining the location, the site of substitution and the valence state of Fe in clay minerals (Karickhoff and Bailey, 1973). However, one of the most commonly used applications is in the determination of the number of plates in a montmorillonite tactoid (Shainberg and
Kaiserman, 1969; Frenkel and Shainberg, 1981; Schramm and Kwak, 1982; Ben-Dor and Singer, 1987).

From the OD two parameters can be estimated, the major particle dimension and the number of plates per tactoid. The results of this experiment are presented in Table 4.5. The OD was determined for the mt, mt50 and mt100 in the Ca- and Lisaturated form in three pH ranges. In Table 4.5, acidic pH refers to the OD measured in the pH range 3.5-4.0, neutral 6 5-8.0 and basic 9.2-10.0.

The major particle dimension for the Li saturated samples varied from 2.28 to 2.34 and no significant difference was found upon hydroxy Al coatings. The number of plates per tactoid was found to be independent of pH. The number of plates for Ca-mt were 3.8, 4.3 and 3.9 and these are in the range found in the literature (2.7 to 7.0). For the Ca-mt50, they were 3.0, 3.3 and 3.5, and for the Ca-mt100, 1.8, 1.9 and 1.8. The major difference was the decrease of the number of plates per tactoid upon hydroxy Al coating. This is in contradiction of the work of Shomer and Mingelgrin (1978) who reported aggregates formed by tactoids having about 25 plates per tactoid for Al-montmorillonite versus 16.1 for Camontmorillonite and 1.4 for Na-montmorillonite, using transmission electron microscope (TEM) observations. However in their paper, the clay was only saturated with Al compared to our study where the Al is precipitated onto the surface of the montmorillonite.

| Najor particle dimension              |             |              |              |  |  |  |
|---------------------------------------|-------------|--------------|--------------|--|--|--|
| Sample                                | Acidic (pH) | Neutral (pH) | Basic (pH)   |  |  |  |
| Calcium Mt                            | 2.51 (3.75) | 2.60 (7.98)  | 2.61 (10.02) |  |  |  |
| Calcium Mt-50                         | 2.55 (3.82) | 2.58 (6.70)  | 2.63 (9.45)  |  |  |  |
| Calcium Mt-100                        | 2.66 (3.86) | 2.69 (6.49)  | 2.65 (9.41)  |  |  |  |
| Lithium Mt                            | 2.28 (3.66) | 2.29 (7.38)  | 2.25 (9.99)  |  |  |  |
| Lithium Mt-50                         | 2.29 (3.81) | 2.28 (6.98)  | 2.24 (9.69)  |  |  |  |
| Lithium Mt-100                        | 2.28 (3.95) | 2.32 (7.44)  | 2.38 (9.25)  |  |  |  |
| Relative number of plates per tactoid |             |              |              |  |  |  |
| Calcium Mt                            | 3.8         | 4.3          | 3.9          |  |  |  |
| Calcium Mt-50                         | 3.0         | 3.3          | 3.5          |  |  |  |
| Calcium Mt-100                        | 1.8         | 1.9          | 1.8          |  |  |  |

Table 4.5 Major particle dimension and number of plates per tactoid derived from optical density measurement

Tactoids of Ca-montmorillonite are formed by repulsive forces between two montmorillonite particles resulting in a large interlayer space. The particles or plates are assumed to be in parallel stacking along the c-axis, forming a faceto-face association, compared to Na-montmorillonite that has a card house structure with edge-to-face association (Rand et al., 1980).

## 4.4 Conclusion

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In this experiment, even with Al-coatings, the titration curves do not identify a cross over point needed to determine the PZSE of the oxide coatings. Consequently, the model of Uehara and Gillman (1980) is not applicable. The PZSE of the synthetic Al-oxide was found at pH higher than 8 implying that below this pH the Al oxide must have a net positive surface charge. From the surface charge measurement by ion adsorption on the montmorillonite coated with Al-oxide, no significant increases in the AEC have been observed. Consequently, the surface properties derived from the pure oxide cannot be applied when the oxide forms a coating.

The backtitration method provides a good fit to the data of the ion adsorption method; in contrast, the traditional potentiometric titration method produces pH-dependent curves that can not be interpreded in terms of net surface charge. This result implies that the backtitration method can be used to measure the pH-dependent surface charge of а montmorillonite sample with and without coatings. This technique has the advantage of being faster than the ion adsorption method and gives meaninful and interpretable data in contrast to the potentiometric titration method.

## 4.5 References

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CHAPTER V

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GENERAL CONCLUSIONS

5.1 Summary

The development of a technique to measure the surface charge of soil colloids must meet two criteria. The first is maximum accuracy of the analytical technique, and the second minimum time needed to perform the analysis. In chapters II and III a backtitration technique was developed, similar to that of Schulthess and Sparks (1986), to measure the pHdependent net surface charge of different soil horizon samples. The results of this technique are in good agreement with those obtained by the ion adsorption method. Moreover, the backtitration technique permits the evaluation of the surface ionization constants for H⁺ exchange and the maximum or total surface charge of particular soil components. These parameters are evaluated graphically and statistically. From these measurements it was concluded that the pH-dependent surface charge of the soil can be computed with reasonable precision from knowledge of certain soil chemical properties. In addition, the backtitration technique has the advantage of correcting for the amount of dissolved ions that may hydrolyze in solution and interfere with surface charge measurement.

The backtitration technique was also applied to the surface charge measurement of montmorillonite, Al-oxide and chemical mixtures of the two. It was found that a good match

is obtained when the results of this technique were compared to those of the ion adsorption method for relatively pure minerals.

In this experiment, the model of Uehara and Gillman (1980) and Gillman and Uehara (1980) fails to determine the permanent charge of the montmorillonite coated with Al-oxide. The major argument of their method was that at the cross over titration curves point of in different electrolyte concentrations (PZSE), the permanent charge of a mixture can be determined. As demonstrated in chapter IV, we cannot use this PZSE for the chemical mixtures in this study, because no PZSE was defined. Consequently the validity of the Uehara and Gillman model (1980) is in doubt.

The reduction of surface charge upon Al-oxide coating or hydroxy-Al interlayer formation of smectite is commonly accepted in the literature (Kozak and Huang, 1971; Meyers and Ahlrichs, 1972; Keren et al., 1977; Keren, 1986). Chapter IV of this thesis shows the contrary. It is the first time that this behavior has been reported in the literature. This is observed because in this study, the pH-dependent CEC by ion adsorption has been measured on the chemical mixture, compared to the other study where mechanical mixtures are used (Madrid et al., 1984; Madrid and Diaz-Barrientos, 1988, Madrid et al., 1989).

5.2 Future Research

The development of the backtitration technique and the increase in the surface charge of a montmorillonite upon Aloxide coating, opens the way to future research. First, backtitration could be tested for use on the study of the adsorption of heavy metals in soils. This could be done by adding a solution containing heavy metal at pH 3, when the acid titration is finished in the backtitration procedure, just before backtitrating, and also doing the same thing with the reference solution. This kind of experiment will permit the development of new methods to assess the sorption of heavy metals in soils.

The backtitration technique presented in this thesis was tested at different soil:solution ratios, equilibrium times and titration rates in $0.005 \text{ M} \operatorname{Ca}(\operatorname{NO}_3)_2$. It would be an advantage to try different electrolyte solutions to verify their effect on the behavior of the pH-dependent surface charge, and if they give the same log K values for the surface protonation constants and maxima of adsorption.

The results presented in the chapter IV lead to the development of two ideas for future research. The first is related to the effect of Al coatings on montmorillonite. Because of the activation of surface charge upon acid/base addition, the existence of exchangeable H⁺ could be investigated. It is possible that the exchangeable H⁺ is not

exchangeable with common cations, i.e. Ca²⁺, Mg²⁺, Na⁺, K⁺, etc. but rather it reacts directly when in contact with H⁺ and OH⁻ This view of the problem leads to a more in solution. complicated one: The notion of titratable acidity in soils and clays. According to the arguments presented here, it is possible that exchangeable acidity as H⁺ cannot be assessed by the well accepted titratable acidity method (Peech et al., 1962), that is by definition the acidity exchanged with BaCl_tetraphenylboron at pH 8.1, but rather the difference in CEC by the H⁺ that can be removed or replaced upon base addition, without changing the soil or suspension pH. If this hypothesis is demonstrated, it will imply a new definition of the exchangeable H^* .

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This notion can be understood by visualizing the normal procedure of ion adsorption method to determine the CEC of a suspension. In almost all the ion adsorption methods, the pH must be adjusted to a certain pH in a high concentration of electrolyte. For example, adding base or acid to adjust a suspension, originally at pH 5.0, will require x mL of base to reach a pH of 7.0. However, to obtain this solution pH, we have to readjust the pH after a certain amount of time. This is due to the buffer capacity of the soil that consumes the excess of OH⁻ added. It is possible that the amount of OH⁻ added, neutralized by the soil, without changing its original pH is the real amount of exchangeable H⁺.

The backtitration technique described here could be

improved by incorporating a mathematical or chemical model using definitions of different planes of adsorption as defined in the surface complexation models (Westall et Hohl., 1980). In this case it will be possible to have a complete model, considering both multisites and multilayers of adsorption.

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APPENDICES

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Appendix I

Total chemical analysis of the Ap and Bg horizons.

| No | Horizon | SiO2 | Al ₂ 0 ₃ | Fe ₂ 0 ₃ | MgO |
|------|---------|------|--------------------------------|--------------------------------|-------------------|
| | | * | X | x | x |
| 5 | Ap | 51.8 | 16.4 | 7.60 | 2.69 |
| 6 | Bg | 53.9 | 17.4 | 8.63 | 3.27 |
| 7 | Ap | 51.6 | 15.2 | 6.52 | 2.72 |
| 8 | Bg | 57.9 | 16.4 | 7.01 | 3.07 |
| 9 | Ap | 54.8 | 16.1 | 7.53 | 2.21 |
| 10 | 8g | 54.7 | 17.6 | 8.23 | 2.64 |
| No | Korizon | ti02 | MnO | κ ₂ 0 | Na ₂ O |
| | | × | x | x | xx |
| 5 | Ар | 0.72 | 0.14 | 2.64 | 1.55 |
| 6 | Bg | 0.74 | 0.10 | 2.93 | 1.85 |
| 7 | Ap | 0.72 | 0.10 | 2.53 | 1.63 |
| 8 | Bg | 0.75 | 0.09 | 2.71 | 2.08 |
| 9 | Ар | 0.74 | 0.14 | 2.57 | 1.59 |
| 10 · | Bg | 0.75 | 0.15 | 2.64 | 1.59 |
| No | Horizon | P205 | LOI | v | Cr203 |
| | | × | <u>x</u> | ppm | ppm |
| 5 | Ap | 0.19 | 14.4 | 100 | 213 |
| 6 | ßg | 0.16 | 9.51 | 103 | 279 |
| 7 | Ap | 0.24 | 16.8 | 90 | 187 |
| 8 | Bg | 0.17 | 7.73 | 96 | 194 |
| 9. | Ap | 0.19 | 12.8 | 106 | 216 |
| 10 | Bg | 0.11 | 10.5 | 109 | 222 |
| No | Horizon | CaO | Ni | 8a0 | |
| | | x | pom | mqq | |
| 5 | Ар | 2.44 | 100 | 807 | |
| 6 | Bg | 2.34 | 139 | 819 | |
| 7 | Ар | 2.44 | 63 | 795 | |
| 8 | Bg | 2.52 | 76 | 885 | |
| 9 | Ap | 1.91 | 85 | 745 | |
| 10 | Bg | 1.66 | 76 | 827 | <u> </u> |

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X-ray patterns of the mt sample.





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X-ray patterns of the mt50 sample.





X-ray patterns of the mt100 sample.





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X-ray patterns of the synthetic Al-oxide.



X-ray patterns of the mt sample following the Greene-Kelly test.



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Infrared spectra of the mt, mt50, mt100, Li-fixed mt and the synthetic Al oxide, (400 to 1200 cm^{-1})





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Potentiometric titration of the synthetic Al oxide in $Ca(NO_3)_2$.

pH-dependent sedimentation volume for the mt, mt50 and mt100 samples.

