

THE INFLUENCE OF ALUMINIUM ON NEGATIVE SOIL CHARGE

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Abstract. The influence of pH and aluminium on soil clays' negative charge was investigated for clays separated from acidic soils of different origin. It was observed that aluminium caused a negative charge decrease due possibly to nonexchangeable Al polycations adsorption in the 4-6 pH range. Aluminium complexing by organic matter can diminish soil negative charge in a broad range of pH.

INTRODUCTION

Chemically active aluminium may occur in soils in different forms [11] which are governed mainly by the pH of the soil solution and the soil mineral composition [2,6,8]. Trivalent aluminium ions are present in soils at low pH values and they hydrolyse and polymerize as pH increases [1,4,5]. Because of the high mass and charge of the polycations, they are preferentially adsorbed by negatively charged soil surfaces [11] and are weakly exchangeable or nonexchangeable which causes blocking of the soil negative charge [7]. As pH increases further, when the OH/Al ratio reaches 2.2-2.4, the polycations are transformed into polymers of high molecular weight and low charge per Al atom, leading to the formation of amorphous or crystalline aluminium oxide [10].

Soil aluminium is strongly bonded on soil organic matter mainly by the organic matter's strongly acidic functional groups [9]. This leads to the decrease of negative charge

for the organic matter. Soil organic matter fully saturated with aluminium exhibits an apparent point of zero charge [3].

The purpose of the present work was to observe the influence of pH-aluminium relations on soil clay fraction negative charge.

MATERIALS AND METHODS

The material studied consisted of six clay fractions separated from acidic soils of different origin. The characteristics of the soils and their clay fractions are given in a previous paper [12].

From clays, the organic matter, iron oxides and aluminium oxides were removed and subsequent samples were converted into homoionic sodium forms with the methods presented in a previous paper [12].

Suspensions of natural clays as well as clays after completion of the removal procedures were adjusted to pH 3 with 0.01 N HCl and after two weeks they were converted into aluminium forms, by duplicate equilibration with a N AlCl₃ solution following by centrifuging and equilibrating the sediment five times with a 0.005 N AlCl₃/0.005 N NaCl pH 3 solution. A final clay to solution ratio of 1:10 was established. Samples of clay suspensions obtained were adjusted to different pH values with a 4 N NaOH/0.01 N NaCl solution and after two weeks the

exchangeable ions were extracted with a N BaCl₂ solution. After exchangeable ion removal, the sediments were equilibrated five times with 0.01 N BaCl₂ solutions of pH's equal to the pH values of the given samples followed by exchangeable barium ion determinations (N LaCl₃ extraction, AAS measurements).

RESULTS AND DISCUSSION

Measured herein quantities of exchangeable barium were taken as the values of negative surface charge of clays in aluminium forms and they are presented in Table 1. These values were different from the values measured for clays of the same samples in sodium form which were presented in a previous paper [13].

Comparing the above mentioned data it can be seen that the charge of aluminium form clays is lower than that of sodium form clays for natural clay samples over the entire pH range. This is probably caused by the strong adsorption of aluminium by soil

organic matter leading to blocking of part of the organic matter charge.

For the samples containing no organic matter (with the exception of 3D and 5D samples), the following tendency is observed: below pH 4, surface charge for both aluminium and sodium forms is equal; in the pH range from 4 to 6, aluminium form charge is significantly lower than the charge of sodium forms; and above pH 6, the charge of aluminium form tends to be slightly higher. For 3D and 5D clays, aluminium form charges are lower than sodium form charges up to pH 6.

This phenomena may be explained by taking into account the pH dependent behaviour of aluminium. Below pH 4, aluminium occurs as exchangeable trivalent ions. They can be totally desorbed by barium ions and the measured barium adsorption does not depend on the ionic form of the given sample. In the pH 4 to 6 range, the decrease of aluminium form charges in comparison to sodium form charges may be due to nonex-

Table 1. Quantities of negative surface charge, (cmol n⁻¹kg⁻¹), on aluminium forms of the clays investigated, at different pH values

pH	1A	1B	1C	1D	2A	2B	2C	2D	3A	3B	3C	3D
3.0	22.5	24.0	24.7	26.1	21.9	20.2	22.5	25.2	46.4	45.1	49.0	54.2
3.5	24.3	25.2	26.8	28.3	22.4	20.4	23.0	25.5	49.3	47.5	51.1	55.9
4.0	29.0	27.8	29.0	30.1	23.8	21.1	23.2	26.0	55.8	48.8	53.5	57.7
4.5	32.6	25.9	27.2	28.9	25.2	20.1	22.2	24.3	58.5	46.4	50.1	55.4
5.0	34.4	24.1	25.8	27.2	27.7	19.4	21.6	23.4	63.0	45.1	48.9	52.8
6.0	47.3	31.3	32.1	32.8	36.7	22.4	24.3	26.8	80.3	54.0	60.2	64.6
7.0	59.5	33.8	33.4	34.1	43.1	23.8	25.0	27.9	91.5	59.5	64.1	66.6
8.0	72.1	35.5	34.9	35.4	49.1	26.7	25.7	28.6	101	63.2	66.7	68.7
8.5	79.8	36.2	35.6	35.2	53.1	28.4	26.9	29.0	107	64.9	68.2	69.5
pH	4A	4B	4C	4D	5A	5B	5C	5D	6A	6B	6C	6D
3.0	22.9	22.0	23.0	24.3	36.1	40.3	44.2	46.7	16.1	15.5	17.6	21.9
3.5	23.9	22.3	23.4	24.4	38.9	41.6	45.1	47.1	17.2	15.5	18.0	22.0
4.0	28.5	22.6	24.3	24.9	41.8	42.5	45.7	48.9	17.9	15.9	18.5	22.8
4.5	31.1	21.5	23.2	23.5	42.6	41.2	43.6	48.6	18.3	15.0	17.9	22.3
5.0	33.6	20.4	22.7	22.5	44.4	39.9	41.6	45.0	19.4	14.4	17.1	21.4
6.0	44.3	25.1	26.8	26.9	56.3	44.6	47.2	51.4	27.0	17.1	20.6	24.8
7.0	57.5	27.6	28.1	28.9	62.5	46.9	49.4	53.3	31.2	18.0	21.7	25.8
8.0	71.1	29.7	29.4	30.1	69.2	48.8	52.1	54.9	33.8	21.6	23.4	26.3
8.5	80.8	31.5	30.5	30.3	71.7	50.7	52.8	56.1	36.5	22.6	24.8	27.2

Explanations: 1-Mollic Gleysol; 2- and 3- Eutric Cambisols; 4-Stagnogleyic Phaeozem; 5-Orthic Luvisol; 6-Podzoluvisol. A-natural clays; B-after organic matter removal; C-after Fe removal; D-after Al removal.

changeable aluminium polycations adsorption, leading to negative charge blocking. The increase of aluminium form charges over sodium form charges above pH 6 may be attributed to the input of newly precipitated aluminium oxides to the total negative sample charge. The presence of smectites in clays 3 and 5 (see [12]), and the entering of Al into interlamellar spaces can explain the lowering of charge in aluminium forms of the 3D and 5D samples at low pH values.

CONCLUSIONS

1. Aluminium caused a negative charge decrease due to nonexchangeable Al polycations adsorption in the 4-6 pH range.

2. Aluminium complexing by organic matter can diminish soil negative charge in broad range of pH.

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WPLYW GLINU NA UJEMNY ŁADUNEK POWIERZCHNIOWY GLEBY

Badano wpływ pH oraz glinu glebowego na wielkość ujemnego ładunku powierzchniowego na wybranych frakcjach ilastych wydzielonych z gleb o charakterze kwaśnym. Zaobserwowano, iż obecność glinu powoduje obniżenie ujemnego ładunku powierzchniowego w zakresie pH od 4 do 6, co może być spowodowane niewymienną adsorpcją polikationów glinu. Kompleksowanie glinu przez glebową materię organiczną powoduje obniżenie jej ładunku w szerokim zakresie pH.