HIGH EXCHANGEABLE SODIUM SATURATION OF SOIL DOES NOT ALWAYS INDUCE HIGH ALKALINE REACTION

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ABSTRACT

The pH study of artificially prepared soils having at the same time exchangeable Na and H in the soil colloidal complex, showed that these soil samples have an acid to slight alkaline reaction (pH = 4.8-8.3), unlike native soils (without exchangeable H), that have a high alkaline reaction (pH = 8.5-10.0). For these base unsaturated soils the following relation is valid: $Ph = -0.0005V_{Na}^2 + 0.0931V_{Na} + 4.4581$. This equation shows that pH values in the acid-neutral domain are maintained even for very high percentage of exchangeable Na. The multiple relation between pH on one part and V and V_{Na} on the other is the following: $pH = 0.026V + 0.033V_{Na} + 4.20$; an increase of V_{Na} with 10% corresponds to an increase with 0.33 pH units and an increase of V with 10% (or decrease of V_H with 10%) corresponds to an increase of 0.26 pH units. The pKs calculated from the last equation is about 5.50. In the case of saturated soils having different degree of exchangeable sodium, the relation for pH-V_{Na} is: $pH = 0.031V_{Na} + 8.58$; one can see that an increase of V_{Na} with 10% results in a pH increase with 0.31 units, very close to that of base unsaturated soil. The soils polluted with brines can have a more acid reaction than the reaction of the soil samples presented in the paper, due to the presence of NaCl (exchange acidity in unsaturated soils or especially saline effect in saturated soils). Consequently, a revaluation of the genetic and diagnostic signification of the V_{Na}, as well as of its significance from land improvement point of view is necessary. It is also adequate to study the plant nutrition influence of the soil having at the same time various high saturation degrees of cation exchange capacity both for exchangeable sodium and exchangeable hydrogen.

Key words: soil pH, base unsaturated and saturated soils, exchangeable Na, soils polluted with brines.

INTRODUCTION

Natural soils have normally low exchangeable Na saturation, generally below 2-5% of CEC (cation exchange capacity). In these base saturated soils, for example in calcaric chernozems from steppe zone of Romania, the proportion of adsorbed cations in the soil colloidal complex is the following: Ca 80%, Mg 15%, K 2.5%, and Na 2.5% of CEC (Cernescu, 1961), on an average; the reaction (pH) of these soils is 8.1-8.5.

The high alkaline reaction with pH over 9.0 is only present in sodic soils (solonetz and sodic subtypes of various soil types), soils which are characterized by a high percentage of exchangeable Na in the colloidal complex, generally more than 10-15% of the CEC (sometimes with soda) and which – in natural conditions of formation – are practically without exchangeable H. From this reason, the high alkaline soil reaction was associated with high exchangeable Na saturation of soil (which sometimes leads to soda coming out).

Nowadays, as a consequence of the acid soil pollution with brine from the oil extraction installations, soils having at the same time considerable percentages of exchangeable H* and Na appeared. Though these soils have a high exchangeable Na saturation, they however present a strongly acid reaction (Latis et al., 1996, Toti et al., 1996). This finding does not correspond to the recognized knowledge, generalized from the existing data regarding the soils developed in the natural conditions.

In order to clarify if this strongly acid reaction of soils is due to cationic exchange reaction between NaCl and exchangeable H from soil, or to hydrolysis of unsaturated soil (with exchangeable H), the authors have done an experimental laboratory study. The results were published in two papers in *Stiinta Solului* (*Romanian Journal of Soil Science*), *vol. XXXVIII, 2004, no. 1-2*. Based on these data we present here the relation between soil reaction (pH), on one hand, and soil exchangeable Na and H saturation, on the other hand.

* H is considered as soil total acidity, representing $H^+ + Al^{3+}$

MATERIAL AND METHODS

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We used acid soils (luvisols and cambisols) and saturated soils (chernozems) for the preparations of soil samples with different proportions of Ca^{2+}, Na^{+} and H^{+} in the composition of the cationic exchange capacity (CEC), by a treatment with various quantities of $NaHCO_3$, $CaCO_3$ and NaCl (in last case followed by a leaching of chlorides from soil) (for details, see Florea and Rizea, 2004, and Rizea and Florea, 2004).

From the soil samples prepared this way, the following soil characteristics were determined: pH in water, pH in KCl saturated solution, exchangeable Na, exchangeable H, CEC and, by calculation, Na saturation degree, V_{Na} (from CEC) and H saturation degree, V_{SH} (from CEC) and implicitly base saturation degree, V, of each soil sample; V_{SH} corresponds, evidently to 100-V (ICPA, 1986). Obtained results are presented in Tables 1 and 2. Data from Tables 3 and 4 emphasize the influence of NaCl added in soil.

RESULTS AND DISCUSSION

Experimental data are examined and discussed separately for the base unsaturated and base saturated soils (generally with $CaCO_3$), because soil chemical reactions and equilibriums are completely different in the two cases.

a. Base unsaturated soils without salts (easily or heavily soluble)

From the Table 1 data, one can discriminate two categories of soils according to their pH-V_{Na} values pairs, the first one in which V_{Na} has values less than 5%, corresponding, generally, to unaffected salt soils with neutral to acid reaction depending on the V_{SH} values, and the second one in which V_{Na} has values higher than 5%, with only slightly alkaline to acid reaction; this last category differs obviously from sodic soils (that have a high alkaline reaction) due, of course, to the influence of exchangeable H as component of the CEC.

Table 1. Some characteristics of soil samples with different percentages of exchangeable Na and H (prepared in laboratory)

Sample number	pH (H_2O)	pH (KCl)	V_{Na}	V_{SH}	V
			% from CEC		%
1	5.11	3.95	1.6	57.4	42.6
2	5.70	4.24	9.1	53.5	46.5
3	6.40	4.78	20.2	40.5	59.5
4	7.45	5.49	30.3	32.0	68.0
5	7.55	6.15	37.0	26.2	73.8
6	7.96	6.45	46.2	16.1	83.9
7	8.30	7.03	51.5	9.8	90.2
8	5.24	4.24	1.6	53.1	46.9
9	5.61	4.83	1.5	42.4	57.6
10	6.00	5.28	1.6	33.2	66.8
11	6.36	5.74	1.5	27.9	72.1
12	6.87	6.24	1.6	17.7	82.3
13	7.05	6.31	1.7	11.5	88,5
14	4.80		5.2	56.2	43.8
15	5.19		8.2	56.3	43.7
16	5.26		11.6	53.8	46.2
17	5.36		12.8	54.6	45.4
18	5.44		16.4	53.3	46.7
19	5.34		16.9	51.9	48.1
20	4.53		0.2	96.8	3.2
21	5.77		14.7	80.8	19.2
22	6.20		27.7	68.5	31.5
23	6.86		45.0	50.4	49.6
24	7.62		57.9	37.8	62.2
25	4.95		2.2	95.2	4.8
26	4.71		3.4	93.6	6.4

27	4.48		2.9	94.1	5.9
28	4.50		3.4	93.2	6.8

For both categories of soils, the relation pH-V, expressed in the form of Saidel-Cernescu equation (Saidel, 1931; Cernescu, 1940), namely:

$$pH = pKs + \log [V/(100-V)]$$

are graphically presented in Figure 1 by the curves 1 and 2 (pKs being the dissociation constant of soil acidoid).

The form of these curves is similar to the classic one, a fact that strengthens the data confidence. For the first category (unsaturated soils with $V_{Na} < 5\%$), the mathematical relation (1) is:

$$pH = 5.45 + \log [V/(100-V)] \quad (1)$$

and for the second category (2):

$$pH = 5.92 + \log [V/(100-V)] \quad (2)$$

The curve corresponding to the relation 2 is situated above the one corresponding to relation 1, generally with a difference of about 0.5 pH-value. This increase of pH is, evidently, an influence of the presence of higher V_{Na} values (to V_{Ca} values detriment) in the soil CEC. As a consequence, high values of V_{Na} in acid soils result in a low increase of soil pH, but not in a strongly alkaline reaction.

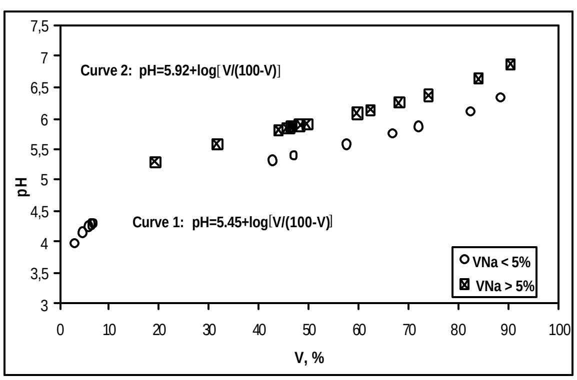

Figure 1. Variation of the pH-values depending on V values for base unsaturated soils with V_{Na} less and more than 5%

In the figure 2 the correlation pH-V_{Na} for the unsaturated soils (samples with different percentage of exchangeable Na) is presented as quadratic equation (3):

$$pH = - 0.0005V_{Na}^2 + 0.0931V_{Na} + 4.4581 \quad (3)$$

From this relation (3) and the curve pH-V_{Na} (Figure 2) it can be seen that for base unsaturated soils, with high Na saturation percentage, the soil reaction values remain in the acid-neutral interval for V_{Na} values until 35% and increase towards pH 8 only at V_{Na} values of 60% (in contrast with base saturated soils). Consequently, the interpretation of the V_{Na} values from the genetic and land improvement point of view, as well as diagnostic criterion, must be reconsidered according to these data.

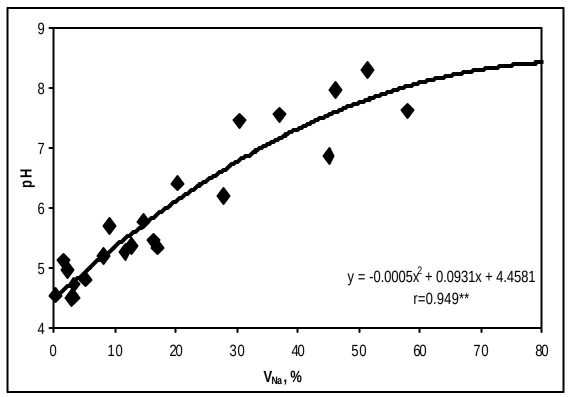

Figure 2. Variation of pH-values depending on V_{Na} for the base unsaturated soils

Processing the presented data for pH, V and V_{Na} the following two multiple relations (complementary) resulted for 25 degrees of freedom and a correlation coefficient of a 0.945:

$$pH = 0.026V + 0.033V_{Na} + 4.20 \quad (4a)$$

$$pH = - 0.026V_{SH} + 0.033V_{Na} + 6.80 \quad (4b)$$

From these relations one can find an increase of pH with 0.33 units for an increase of V_{Na} with 10% and an increase of pH with 0.26 units for an increase of V with 10% (or a decrease of V_{SH} with 10%). It seems that exchangeable Na influence on pH is a little higher than that of the exchangeable H.

For the V = 50% and $V_{Na} = 0$, from the equation (4a) results the value 5.5 for the pH that corresponds to pKs (dissociation constant of soil acidoid); this value of the pKs is very close to the ones known from literature: 5.1-5.8 (Cernescu, 1942; Florea et al., 1964). It is to point out that the equations (4a) and (4b) are valid for V_{Na} values between 5 and 90% and V_{Na} less than 60%.

b. Base saturated soils (with lime, without soluble salts)

The experimental data in the case of base saturated soils (Table 2 and Figure 3) – soils without exchangeable H corresponding to natural conditions – show a clear increase of the pH values, from 8.5 to 10.7, as the exchangeable Na saturation increases. This increase of pH values is very rapid for the V_{Na}<10% and very slow for V_{Na}>10%, tending asymptotic to values about 11 (fact confirmed in natural conditions).

Table 2. Some characteristic of calcaric soil samples with different percentage of exchangeable Na (prepared in laboratory)

Sample number	pH (H_2O)	V_{Na} % from CEC	V %
1	8.54	2.5	100
2	9.14	18.2	100
3	9.69	23.3	100
4	10.39	37.7	100
5	10.50	50.5	100
6	10.72	86.4	100
7	8.77	8.1	100
8	8.86	8.9	100
9	8.59	10.3	100
10	8.65	10.2	100
11	8.67	10.0	100

For the base saturated soils, the relation between pH and V_{Na} is the following:

$$pH = 0.031V_{Na} + 8.58 \qquad (5)$$

Also, in this case a variation of 10% of V_{Na} induces a pH modification that is very close to those specified before (0.31 versus 0.33). But, the variation of pH - values is much better reflected by the following logarithmic equation (Figure 3):

$$pH = 1.8 \log V_{Na} + 7.17 \qquad (6)$$

The idea of these laboratory studies was generated by the appearance of soils polluted with brine, having both exchangeable Na and exchangeable H. But the soil samples prepared in laboratory with different ratios of exchangeable Na and H do not correspond exactly to the situation of brine polluted soils, because these soil samples contain a certain quantity of NaCl at least in the first phase of pollution; this amount of NaCl causes a cationic exchange reaction with formation of HCl, so that they have a reaction much more acid than those presented in the paper. This finding is confirmed by the Table 3 data, from which one can see that pH values of soil samples treated with NaCl and then leached are higher than pH values of the same soil samples treated with NaCl and unleached and these ones are higher than pH values in KCl solution (1 n).

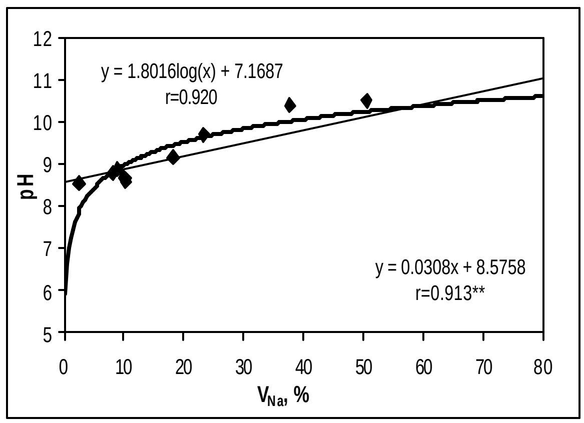

Figure 3. Variation of pH-values depending of V_{Na} for the base saturated soils

Table 3. The pH-values of base unsaturated soil samples with different percentages of exchangeable Na and H

Sample number	pH* (H_2O)	pH** (H_2O)	pH *** (KCl)
1	5.19	4.75	4.05
2	5.26	4.63	3.99
3	5.36	4.67	4.08
4	5.44	4.57	4.03
5	5.34	4.54	4.04
6	4.80	4.85	4.04
7	4.71	3.98	
8	4.95	4.45	
9	4.48	3.88	

10	4.50	3.90	

* water pH values of treated with NaCl soils and leached of NaCl (with alcohol);
** water pH values of treated with NaCl soils and unleached of NaCl;
*** pH values in KCl solution, 1 n.

Also, in the case of calcareous soils, the pH values of soil samples having salts (NaCl) will be lower than pH values of soil samples without salts (Table 4), as a consequence, especially, of saline effect.

Table 4. The pH-values of calcaric soil samples with different percentages of exchangeable Na

Sample number	pH* (H_2O)	pH** (H_2O)
1	8.77	7.96
2	8.86	7.96
3	8.59	7.82
4	8.65	7.87

* water pH values of treated with NaCl soils and leached of NaCl (with alcohol);
** water pH values of treated with NaCl soils and unleached of NaCl.

CONCLUSIONS

The artificially prepared soil samples having high percentage of exchangeable Na (of CEC), but also exchangeable H, have an acid to slight alkaline reaction (pH = 4.8-8.3), unlike native soils that have - in the lack of exchangeable H - a high alkaline reaction (pH = 8.5-10.0).

For these base unsaturated soil samples with V_{Na} less than 5 % the relation (1) is valid:

$$pH = 5.45 + \log [V/(100-V)] \quad (1)$$

but for those with V_{Na} higher than 5 % the relation (2) applies:

$$pH = 5.92 + \log [V/(100-V)] \quad (2)$$

The presence of the exchangeable Na concomitantly with exchangeable H in CEC induces only a weak increase of pH values (with about 0.5 units).

For these base unsaturated soils having high percentage of exchangeable Na, the following relation is valid:

$$pH= - 0.0005V_{Na}^2 + 0.0931V_{Na} + 4.4581 \quad (3)$$

This equation (see also Figure 2) shows that pH values are maintained in the acid-neutral domain even for very high percentage of exchangeable Na. For example, at 40-50% exchangeable sodium saturation, the pH values remain below 7.38-7.86 (simulating the state of acid soils polluted with brines).

For the artificially base unsaturated soils, the multiple relation between pH on one hand and V and V_{Na} on the other is the following:

$$pH = 0.026 V + 0.033 V_{Na} + 4.20 \quad (4)$$

An increase of V_{Na} with 10 % corresponds to an increase with 0.33 pH units, while an increase of V with 10 % (or decrease of V_H with 10 %) corresponds to an increase with 0.26 pH units. The pKs calculated from equation (4) is 5.5.

For the base saturated soils the following relation was deduced:

$$pH = 0.031V_{Na} + 8.58 \quad (5)$$

One can see that an increase of V_{Na} with 10 % results in a pH increase with 0.31 units, very close to that of base unsaturated soil. For 40-50% V_{Na} the pH values are between 9.82 and 10.13.

The soils polluted with brines can have a more acid reaction than the reaction of the soil samples presented in the paper, due to the presence of NaCl (exchange acidity in unsaturated soils or especially saline effect in saturated soils).

A revaluation of the genetic and diagnostic significance of the V_{Na}, as well as of their meaning from land improvement point of view, taking into account these findings, is necessary. It is also adequate to study the plant nutrition influence of the soil having at the same time various high saturation degrees of cation exchange capacity, both for exchangeable sodium and exchangeable hydrogen.

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