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OXIDATION OF CLAY MINERALS WITH OXYGENATED WATER

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Abstract

An oxidation method with oxygenated water was used on the separated and calcium saturated clay fractions and were estimated the concentrations of smectite and illite by means of X-ray diffraction patterns. In addition were calculated three crystallinity indices. The illite crystallinity indices are greater than those of smectite and show that illite has greater particles and higher ordering of atoms on broken surface and in lattice structure. This suggest a particle corrosion with a releasing of some structural elements and an accentuation of the illite→smectite transformation.

INTRODUCTION

The alteration processes of soil minerals are surface processes [5] which depend on the stability of each mineral their crystallinity, intensity of microbiological activity, composition and ionic strengh of soil solution, the removing speed of alteration products from the surface mineral proximity, climate conditions.

In the present work were investigated in laboratory the effect of treatment with oxygenated water on the clay minerals by comparison of samples with or without treatment.

MATERIAL AND METHODS

A group of 157 soil samples were selected from main types of soils (chernozem, phaeozem, luvisols, rendzic leptosol, vertisol, arenosol, fluvisol), from all horizons and many Romanian regions (Banat, Oltenia, Muntenia, Moldavia, Transylvania).

The clay fraction were separated by sedimentation from suspensions dispersed with natrium hydroxide at pH 9, saturated by calcium, deposited on glass plates as orientated preparates. An alicot part with 1±0.1 Ca saturated clay in 100 cm^3 suspension were treated with 1 cm^3 oxygenated water and holded a 30 minutes on the boiling water bath. Then the H_2O_2 is removed by a leaching treatment with $CaCl_2$ 1n and deposided on glass plates.

RESULTS AND DISCUSSION

Oxygen is the strongest oxidant in soil, it diffuses from the atmosphere into soil surface horizons and this diffusion is greater when increase the soil aeration porosity. The agricultural technologies increase the air volume into tilled horizons and accentuate the oxidation reactions. But pore distribution is heterogenous in soils and the contact with the minerals is affected on the one hand by alteration pellicles [5] and on the other side deposits which cover the crystallites surfaces and on the other by the aggregation of soil particles.

The oxidation effect on clay minerals were investigated by comparison of concentration and crystallinity indices of untreated and treated samples with oxygenated water. In order to research this reactions were selected 157 samples from the main soil types all horizons and many Romanian regions. Some statistical data are presented in table 1. Kaolinite is not investigated because of its low concentration in clay fractions.

Table 1

Statistical date of the investigated soils

Property	Mean	Minim	Maxim	Median
Smectite and intergrade minerals				
Content untreated	43.94	13.8	80.5	43.9
Content treated	44.52	15.5	76.5	44.3
IA index untreated	0.433	0.254	1.52	0.392
IA index treated	0.422	0.25	1.72	0.385
IB index untreated	0.165	0	0.74	0.11
IB index treated	0.158	0	0.91	0.1
Illite and its interstatifications				
Content untreated	50.12	17.6	75.5	50.6
Content treated	49.53	20	83.9	50.5
IA index untreated	0.925	0.192	2.08	0.877
IA index treated	0.945	0.404	2.13	0.893
IB index untreated	0.501	0.05	0.79	0.53
IB index treated	0.51	0.02	0.79	0.53
IC index untreated	0.372	0.17	0.926	0.341
IC index treated	0.369	0.189	0.98	0.334

The mean values of mineralogic properties are changed only a little by the treatment with oxygenated water (table 1). The smectite content increase with 1.33% and the IA and IB indices decrease with 2.54% and 4.24% respectively while the illite quantity decreases with 1.18% but the IA and IB indices increase with 2.16% and 1.76% and IC index, the interne ordering decreases with 0.81%. These differences would suggest that smectite is altered with release of structural ions in about the same proportions as illite. IA index namely the mean size of mineral decreases with 2.54% and those of illite increases with 2.16% comparable values but not identical which suggest a higher dissolving of smectite accompagned of a transformation in smectite of the illite particles with smaller size. The variation of IB index-atom ordering on the broken surface, shows a higher alteration of smectite and an increasing of illite crystallinity due to transformation in smectite of crystallites with smaller dimensions and more alterated.

The comparison of the averages with the medians from table 1 shows small differences for the smectite (<0.5%) ans of illite concentrations (<0.95%) and greater differences for crystallinity indices of clay minerals. That suggest beside unimodal distribution multiple histograms or/and with asymmetrical ranges.

The smectite concentration of samples treated with oxygenated water correlates very high with the content of untreated samples (n=157, Rpow=0.909***, Rlin=0.907***, F=715). The power curbe with the greatest correlation coefficient is superposed on the representative straight line (figure 1). The representative points are placed very strong along to statistical curves and show that the oxidation effect remains at a low level for all smectite concentration. Nevertheless the treated samples have their concentration greater under 47.6% smectit and smaller concentration than the untreated samples over this content. This would suggest that oxidation would reduce the smectite concentration and release elements from its structure especially at smaller concentrations and greater surface area.

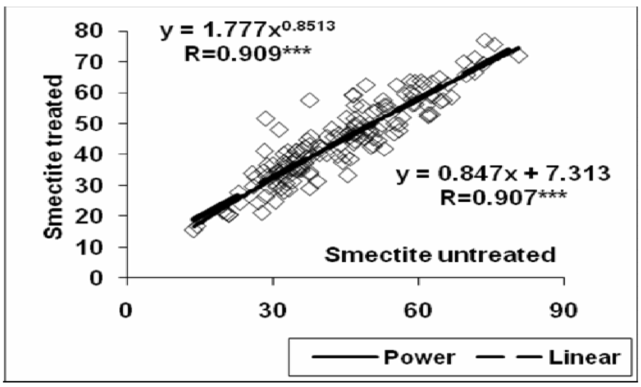

Fig. 1. Effect of treatment on the smectite content

The relation between the mean size of smectite particles (IA) at treated and untreated samples (figure 2) is very high (n=157, Rpoly=0.711***, Rlin=0.704***, F=152) and representative curves are superposed on a large portion of their trajects beginning with the small dimensions where the representative point density is greater. The IA indices of samples with and without treatment are equal for IA=0.395 and show that under this value the particle size of treated samples is greater than those untreated samples and over this the treated samples have smaller values. This suggest that oxidation corrodes the smectite particles and dissolves the smaller particles due to their specific surface area.

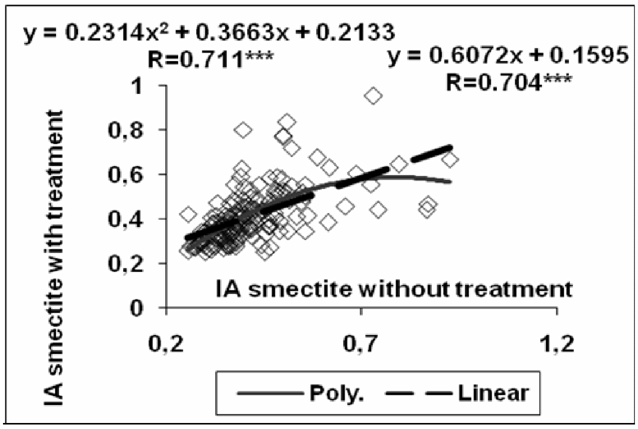

Fig. 2. Effect of treatment on smectite IA index

The smectite IB index of treated particles high correlates with the index of untreated samples (n=157, Rpoly=0.888***, Rlin=0.888***, F=580) and the representative points are placed along to the straight line (figure 3). The atom ordering on the broken surfaces of crystallites has the same value when IB=0.12 for untreated and treated samples. Under this value the ordering is higher for treated and over is higher for untreated samples. This show that all broken surface of smectite particles are corroded in the oxidation processes and at the greatest alterated surfaces are dissolved many structural elements.

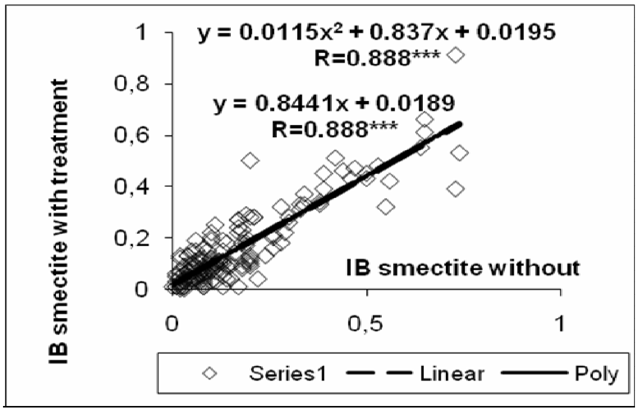

Fig. 3. Effect of oxidation on the smectite IB index

The illite content of treated samples strong correlates with the content of untreated samples (n=157, Rpoly=0.907***, Rlin=0.906***, F=707) and the reprezentative points are placed along to the statistical curve (figure 4). The concentrations are equal at 45.1% illit in clay fraction. Under this value the illite concentrations of treated samples are greater than these untreated and over smaller. This suggest that the oxidation processes release structural ions from crystylline lattice and accentutes transformation reaction illite→smectite of the smallest illite concentration.

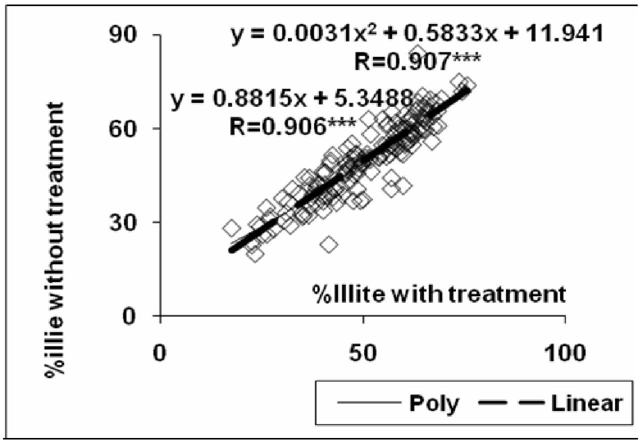

Fig. 4. Effect of oxidation on the illite content

CONCLUSIONS

1. The comparison of statistical mean of mineralogical properties, of their histograms and of relations between the treated and untreated samples show that the elaborated oxidation method modify a little the concentrations and the crystallinity indices of clay minerals with 2:1 structure from Romanian soils.
2. The oxidation increases the smectite concentration and decreases the concentration of illite with about 2%. Under approximatively 45% illite mineral the treated samples have greater concentration than the untreated samples and smaller over this value than untreated samples.
3. Illite has crystallinity indices greater than smectite. This show that illite has particle size greater than smectite, an higher atom ordering on the broken surface and a more ordonate interne crystaline structure.
4. The agricultural technologies increase the oxygen diffusion from atmosphere to soil horizons, intensify the biological activity and the oxidation reaction which release structural ions from clay minerals proportionaly with their surfaces, produces the diminish of their particle sizes but affect a little the interne structure of clay minerals.

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