

INFLUENCE OF SOLID PHASE COMPOSITION AND pH ON AGGREGATION OF SOIL CLAY FRACTION

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Abstract. Relations among clay particle aggregation, clay composition and the pH of equilibrium solution were studied using sedimental scales and sodium forms of clay fractions separated from six acidic soils of different origin. Experimentally obtained sedimentation curves were numerically extrapolated to infinite time and the mass of sediment virtually deposited was taken as a basic factor characterizing aggregation. Aggregation of investigated clays was significantly influenced by the presence of particular solid phase components i.e. organic matter, iron and aluminium compounds, which are apparently connected with their surface charges (negative and positive) and their relative amounts. A pH increase lead to a decrease of aggregation for every case investigated.

INTRODUCTION

Soil microstructure is mainly due to the state of aggregation of soil particles which have the highest degree of dispersion i.e. the clay fraction. Soil aggregation is governed by many factors the most important of which are the sign and value of the surface potential depending on the pH, ionic strength and ionic composition of the equilibrium soil solution. According to the Schulze-Hardy rule, the aggregation influence of the counterion is proportional to sixth power of its valency [14].

Aggregation of soil permanent charge components occurs from the increase of soil

solution concentration which leads to a simultaneous decrease of surface potential and compression of the diffuse double layer [14].

Constant potential component aggregate at their point of zero charge [11] since at this pH the surface potential is zero. At other pH values, the increase of equilibrium solution concentration may also cause constant potential particle aggregation by DDL compression. But at sufficiently high values of surface potential (pH's far from PZC), particles can remain dispersed even at high ionic strengths [5].

Soil organic matter aggregates best at low pH values because of its variable negative charge decrease and its decrease of surface potential [10]. The influence of solution concentration on organic matter aggregation is similar to that on the other soil components.

When interacting particles have opposite sign surface potentials, they aggregate preferentially. Therefore, if under a certain conditions positively charged components (e.g. sesquioxides) are present they form aggregates with permanent charge minerals [1,4] or organic matter [8,9]. Such aggregation may lead to a CEC decrease (charge blocking) [2].

The presence of positively charged edges on clay mineral particles is the reason of their edge to face aggregation under a certain conditions which is microstructure of the cardhouse type [3,12].

The internal structure of soil aggregates depends on the geometry of the interacting particles and their surface charge distribution [13].

The purpose of the present work was to investigate the relationships among clay particle aggregation, clay composition and the pH of the equilibrium solution.

MATERIALS AND METHODS

Materials under investigation consisted of six sodium forms of clay fractions separated from six acidic soils of different origin. The characteristics of the soils and the clay materials are given in a previous paper [6].

Sodium homoionic forms were chosen because of the smallest specific interactions of sodium ions with clays what permits the 'most clear' observations of pH influence on aggregation.

Clay fractions were pretreated in order to subsequently remove organic matter, iron and aluminium oxides. After depletion of particular solid phase components, samples were converted into sodium forms and adjusted to different pH values according to the procedures presented in a previous paper [6]. Every sample was pH adjusted 14 days before sedimental measurement.

Every sample was adjusted to a given pH value and was diluted to a 0.2 % w/w concentration with a solution equivalent in composition and pH to its equilibrium solution. The suspension was placed in a cylinder of sedimental scales and the scale pan was immersed inside it. The mass of sediment deposited on the pan was registered automatically during 24 h of sedimentation.

RESULTS AND DISCUSSION

Stokes law was not applied to the description of the sedimentation curves obtained because the density of the aggregates was

not known. It could not be assumed that the density was the same for aggregates formed at different conditions (i.e. pH) to calculate at least comparative curves of aggregate size distribution. It was because the pH dependent (as also concentration dependent) aggregation changes the internal structure of aggregates (particle orientation), as a consequence, it influences the ratio of solid to solution phases inside the aggregate i.e., the aggregate density. The aggregate has to be treated as an individual particle from point of view of its movement during sedimentation. Therefore, the degree of aggregation was characterized by the fraction of the total solid phase that can virtually settle under the given conditions.

Experimentally obtained sedimentation curves (mass deposited on the scale pan vs. time relationships) were numerically extrapolated to infinite time using the equation

$$m = A - \exp(-bt/c) \quad (1)$$

where m is the mass (kg) of the sediment deposited during the period of time, t (s); A is the mass of sediment deposited virtually, at time equal to infinity; and b and c are curve parameters evaluated by the least square method for a given set of experimental points. In every case, the correlation coefficient for the theoretical curve and experimental points was higher than 0.98.

The A values calculated from the above equation were expressed as a percentage of the total solid phase mass in the suspensions (M) and these values $A \% = (A/M) 100 \%$, were taken as a basic aggregation factor.

The values of A % calculated for the clays investigated are presented in Table 1. The degree of dispersion may be characterized as the part of solid phase that remains in suspension i.e., by $100 \% - A \%$.

It was observed that aggregation of the samples investigated is significantly influenced by the presence of particular solid phase components i.e., organic matter, iron and aluminium compounds. Although it is difficult to find quantitative dependences,

Table 1. Quantities of solid phase able to sediment virtually in infinite time as a percentage of the total content of the solid phase in the investigated clay suspensions (A %) and as related to pH of the equilibrium solution

pH	1A*	1B	1C	1D	2A	2B	2C	2D	3A	3B	3C	3D
3.0	100	100	100	100	100	100	100	100	100	100	100	100
3.5	100	100	100	100	100	100	100	100	100	100	100	100
4.0	100	100	100	100	100	100	100	100	95	100	100	100
4.5	91	100	100	100	100	100	100	100	60	100	100	100
5.0	57	100	88	73	73	100	100	84	37	100	86	100
6.0	38	64	49	46	51	80	69	63	12	61	53	100
7.0	26	29	25	24	38	44	38	36	11	27	24	61
8.0	25	23	21	20	31	33	31	30	10	15	15	16
8.5	24	23	20	19	30	31	30	30	11	15	15	9

pH	4A	4B	4C	4D	5A	5B	5C	5D	6A	6B	6C	6D
3.0	100	100	100	100	100	100	100	100	100	100	100	100
3.5	100	100	100	100	100	100	100	100	100	100	100	100
4.0	100	100	100	100	100	100	100	100	100	100	100	100
4.5	100	100	100	100	84	100	100	100	100	100	100	100
5.0	87	100	97	86	56	100	79	100	77	100	100	100
6.0	53	71	69	78	33	55	42	88	61	85	75	54
7.0	29	38	35	46	25	30	26	32	42	38	35	33
8.0	26	32	31	27	22	21	20	16	34	35	34	33
8.5	26	29	27	25	23	18	20	16	32	34	34	32

* 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.

the qualitative relations are easily observed. It seems that here the surface charges (see refs [6] and [7]) play the most important role.

The least aggregation was for clays containing organic matter. This could be because they had the highest value of negative charge together with the lowest value of positive charge. The repulsive forces in this case would be the highest.

In every case, the increase of positive surface charge quantity lead to an increase of aggregation, as is seen for clays after the removal of organic matter. Samples of given soil clays aggregated to the highest degree when they contained positively charged iron oxides and aluminium oxides. Further removal of iron oxides and then the aluminium oxides weakened aggregation. That was pronounced by the fact that full aggregation ($A\% = 100$) of the respective clays (separated from a given soil) occurred at subsequently lower pH values. Samples 3 and 5 were exceptions of the above dependences. They aggregated better after remo-

val of iron and aluminium compounds than before removal, which may be attributed to edge to face interactions of its main mineral component - smectites.

For different clays at the same pH value, the aggregation was weaker when sample negative charge was higher. This was clearly seen for different natural clays ('A' samples), see Table 1.

It was also seen that a pH decrease caused an aggregation increase. Due to the drop of pH, the variable surface negative charge decreased and simultaneously the positive charge increased, which together lead to an increase in attractive forces.

The sedimentation measured at very high pH values may be attributed not to particle aggregation but rather to sedimentation of coarse particles from the polydispersive suspension.

CONCLUSIONS

1. The influence of the solid phase composition on clay particles aggregation is

connected to their surface charges (negative and positive) and their relative amounts.

2. A pH increase leads to a decrease of aggregation for every case investigated. This can be related to changes of surface variable charge.

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WPŁYW pH I SKŁADU FAZY STAŁEJ NA AGREGACJĘ FRAKCJI KOLOIDALNEJ GLEB

Badano wpływ pH i składu fazy stałej na agregację form sodowych frakcji koloidalnych wydzielonych z gleb kwaśnych o różnym pochodzeniu. Stosowano metodę wagi sedymentacyjnej przy czym do charakteryzowania agregacji stosowano ilość sedimentu, która potencjalnie osiadłaby po nieskończeniu długim czasie osadzania. Zauważono, iż na agregację frakcji ilastych istotny wpływ ma skład fazy stałej, co wydaje się być związane z rodzajami i wielkościami ładunków powierzchniowych. Agregacja we wszystkich badanych przypadkach maleje ze wzrostem pH.