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COLLEGE ON SOIL PHYSICS

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SOIL STRUCTURE

Chapter I: Principal factors in soil structure formation

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CHAPTER I.

PRINCIPAL FACTORS IN SOIL STRUCTURE FORMATION.

1.1. Definition of soil structure.

The primary soil particles do not exist as individuals in the field, but are more or less aggregated into compounds. For sandy soils the association of particles is quite simple. For heavy soils the pattern is more complex. The term "Structure" refers to the spatial arrangements of the primary soil particles.

Soil structure is an important property, because it influences not only the physical conditions, aeration, heat and water economy, but also the availability of plant nutrients, the decomposition of soil organic matter and all the microbiological activities.

Speaking of soil structure as the expression of the spatial arrangements of soil particles, we must distinguish:

a. the spacial arrangement of elementary particles into aggregates and the study of the forces causing or destroying these aggregations. This is the more theoretical aspect of soil structure investigation.

b. the spatial arrangement of the compound soil particles and the pore size distribution resulting from it. This is the more practical aspect of soil structure studies. It includes not only the study of the influence of pore size distribution on soil, air and water economy and on plant growth, but also the methods of finding out the best conditions of the soil physical environment for plant roots.

c. the spatial arrangement and genesis of the compound soil particles as it can be described either in the field (macrostructure) or in the laboratory with the aid of the microscope (microstructure). This is called soil structure morphology. The latter is the meaning given by scientists interested in soil survey, soil classification and soil genesis.

In view of the distinction made above, it is evident that there must be confusion when the term "Structure" is used without further specification.

1.2. Primary particles: structure and physico-chemical properties in general.

The different primary particles composing an aggregate are:

a. non-colloidal: silt, loam, fine sand, sand
b. colloidal: - non cristalline: organic matter and oxydes of silicium, aluminium and iron having different degrees of hydration
  - cristalline: clay minerals and cristallised oxydes or hydroxydes of silicium, aluminium, iron, manganese
c. simple chemical elements: salt, cations, anions
d. water

The colloidal particles are characterised by:

a. very large specific surface i.e. the surface per unit mass
b. special physico-chemical properties

1.2.1. Specific surface.

The total surface per unit mass is called the specific surface S.

$$S = \frac{\text{surface of the particle}}{\text{mass of the particle}}$$

For a particle having a lamellar shape of thickness d cm and length and width of l cm, one obtains: (density ± 2.6 g/cm^3)

- horizontal surface: $2\ l^2$ cm^2
- total surfaces of the sides: $4\ d\ l$ cm^2
- total mass: $2.6\ d\ l^2$ g

so:

$$S = \frac{2\ l^2 + 4\ d\ l}{2.6\ d\ l^2}$$

(as l > 100 d one can neglect 4 d l)

$$S = \frac{2\ l^2}{2.6\ d\ l^2} = \frac{0.8}{d}$$

For a <u>montmorillonite clay</u> with d = 10 Å = 10^{-7} cm, one obtains $0.8/10^{-7} = 8 \times 10^6\ cm^2/g = 800\ m^2/g$.

For an <u>illite clay</u> with d = ± 50 Å, S = 160 m^2/g.

For a <u>kaolinite clay</u> with d = 500 Å, S = 16 m^2/g.

It is to be remarked that in the last case the particle was composed of different flakes; they may sometimes include 50 such units to reach the big size of 500 Å.

On the other hand, the other cristalline particles such as silt, loam, fine sand and sand have an S value of:

- silt ($\bar{d}$ = 15 μ) has an S value of 0.05 m^2/g
- loam ($\bar{d}$ = 35 μ) has an S value of 0.02 m^2/g
- fine sand ($\bar{d}$ = 80 μ) has an S value of 0.01 m^2/g
- sand ($\bar{d}$ = 800 μ) has an S value of 0.001 m^2/g

It is important to remember that a particle having d = 1 μ = 10^{-4} cm, S = 0,8 m^2 or roughly 1 m^2/g.

Using the adsorption technique of N_2 or ethylene-glycol, following values of S have been measured for amorphous colloidal material such as:

- complexes of alumo-silicium: 400 - 500 m^2/g
- amorphous silicium: 100 - 800 m^2/g
- hydrated amorphous aluminium or iron: 100 - 300 m^2/g

In the temperate regions of the globe, the amorphous part of the 0 - 2 μ fraction in the soil does not exceed in general 20 %. In the warm regions, however, this fraction might be very high; especially in very young or in very old soils.

1.2.2. <u>The physico-chemical properties</u>.

Besides th morphological characteristics, attention has to be drawn also on the electrical properties of the surfaces. This, in order to explain the physico-chemical properties which intervene directly in the flocculation, coagulation and aggregation of the particles.

The electrical properties of the surfaces are characterised by the <u>charge density σ</u>. The result is expressed through the numbers of electrons available per $m\mu^2$ (100 $Å^2$).

To get this calculation straight, remember that 1 mole = 1 equivalent of monovalent salt = 6.2 x 10^{23} cations or electron absorbers.

$$\text{charge density} = \frac{\text{number of charges}^{(1)}}{\text{specific surface}}$$

Pure silicium - aluminium - iron hydroxydes have a charge of 0.1 electron per $m\mu^2$. Clay particles and compound silico-aluminium gels have a charge of ± 1.4 electron per $m\mu^2$. This means that the charge unit on the latter colloids occupy a surface of 70 Å. It is important to observe that the charge per unit surface is relatively constant, except for strongly altered soils such as terra-rossa, latosols etc ..., which contain large quantities of sesqui-hydroxydes, of which the charge is changeable in function of the pH. The constant value of σ for clay minerals can be observed on table 1. It is obvious that an increased specific surface goes together with an increased C.E.C. Consequently,per unit surface almost the same charge can be observed.

In the same line of idea's, reference is made to Fig. 1, taken from the work by Beutelspacher and Van der Marel and which gives the summary of a great number of observations.

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(1) The number of charges is equal to the cation exchange capacity (C.E.C.

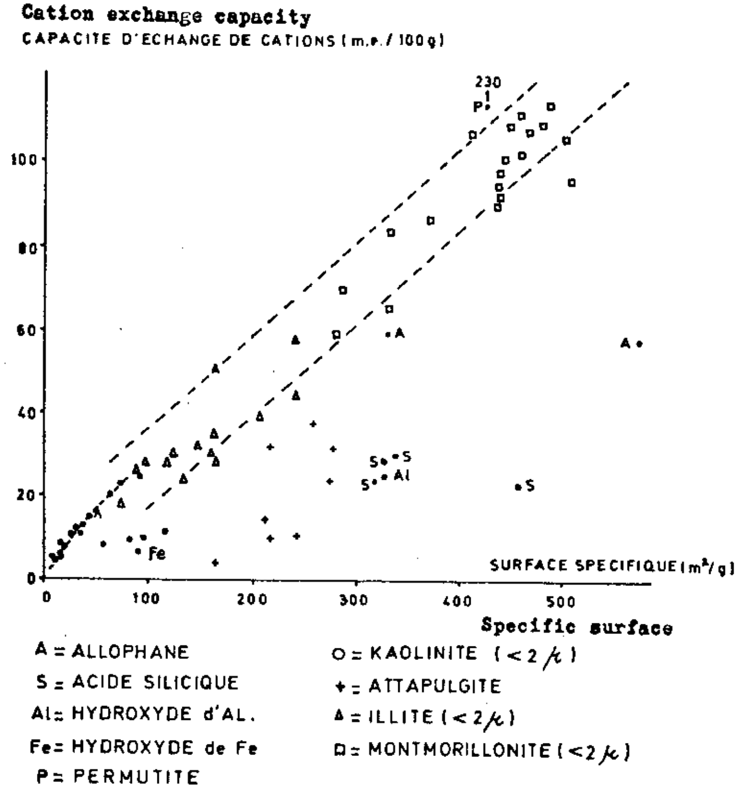


FIG. 1

CEC (me/100 g) ET SURFACE SPECIFIQUE (m²/g) DE DIFFERENTES PARTICULES ARGILEUSES ET MATERIAUX AMORPHES

(BEUTELSPACHER ET VAN DER MAREL)

C.E.C. (meq/100gr) and specific surface (m^2/g) of different clay minerals and amorphic substances

A. Allophane	**o. Kaolinite (< 2 μ)**
S. Silicic acid	**+. Attapulgite**
Al. Aluminium hydroxyde	**Δ. Illite**
Fe. Iron hydroxyde	**□. Montmorillonite (< 2 μ)**
P. Permutite	

Table 1. Characteristics of different colloidal material found in the soil.

Colloidal particles	Specific surface (m^2/g)	C.E.C. (meq/100 g)
Kaolinite	5 - 20	3 - 15
Illite	100 - 200	10 - 40
Mica	100 - 200	20 - 40
Montmorillonite	700 - 800	80 - 100
Sepiolite - attapulgite	100 - 200	20 - 30
Alumo - silicates	300 - 600	± 60

1.2.3. The origin of surface charges.

In order to understand the origin of electrical charges, one must be aware of the structure of clay minerals (see fig. 2). These are divided in four major groups:

1. Two layer types: 1:1 sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons

   $SiO_{4/2}$: silica tetrahedron

   $AlO_{2/4}\ (OH)_{4/2}$: alumina octahedron

   Example: - equidimensional clays: Kaolinite
   - elongate clays: halloysite

2. Three layer types: 2:1 sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral layer

   $SiO_{4/2}$: silica tetrahedron

   $AlO_{4/4}\ (OH)_{2/2}$. alumina dioctahedron

   $SiO_{4/2}$: silica tetrahedron

   Example: - expanding lattice: montmorillonite
   - non-expanding lattice: mica and illite

3. Regular mixed layer types (ordered stacking of alternate layers of different types)

   Example: calorite

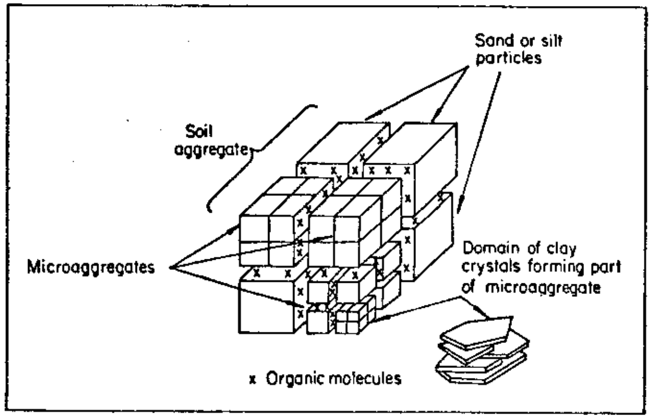


Fig. 2 Schematic illustration of structural organization of soils (85).

4. Chain-structure types (hornblende - like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing aluminium and magnesium atoms
   <u>Example</u>: attapulgite, sepiolite, palygorskite

The formulas used to describe the clay minerals have the following meaning: after the oxydes a fraction is put:

- the nominator indicates the number of molecules surrounding the central ion
- the denominator indicates the fraction of the charge necessary to neutralize the central ion

Besides the cristalized clay particles, amorphous material with the appearance of a gel is also known. As this gel can have once the appearance of glassy material and can change to that with an earthy appearance because of the loss of water, it got the name of "Allophane". The term is derived from Greek words meaning "to appear" and "other" in allusion on the frequent changes just described. Recent studies have shown that also more of this material is crystalline, but that most of it is indeed amorphous to X-ray diffraction. The structure of pure and compound SiO_2 and Al_2O_3 hydrates, which one can find in the soil is still not well known. It is understood that the gels have indeed a regular mesh of which the size is function of the nature and frequency of the ions and the way they were precipitated and formed. The interior is normally accessible to polair ions. The word allophane designates sesquihydroxydes of variable Al_2O_3/SiO_2 ratio's. This type of soils are found mostly in vulcanic area's such as Indonesia, Japan etc...

It is important, however, to recognize that the origin of the charges are in principal the same for the crystalline and non-crystalline mineralogical colloids. The causes of the charges are:

1. Isomorphic replacements. By this one understands the substitutions within the lattice structure of trivalent aluminium for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium for trivalent aluminium in the octahedral sheet. This results in unbalanced charges which are compensated by the adsorption of a cation. This is mostly found on cleavage surfaces, e.g. the basal cleavage surface of the layered clay minerals.

The isomorphic replacement in the octahedral layers are probably the major substitutions causing electrical charges. This process is by far the most important in clays and allophanes having high C.E.C. In compound sesquihydroxydes, the isomorphic replacement is known, but not in pure gels. This explains the low C.E.C. of the latter, but as already said, due to the amphoteric character of the sesquioxydes, the charge is pH dependant.

2. Broken bonds. The broken particles on the edges of the silica-alumina units give rise to unoccupied coordination bonds, which are balanced by adsorbed cations. The broken bonds appear on non-cleavage surfaces and hence on the vertical planes parallel to the c axis of the layered clay minerals and on horizontal planes, perpendicular to the c axis of the elongated clays such as sepiolite - palygorskite - attapulgite minerals. The number of broken bonds increases as the particle size decreases. A special case of broken bonds may be considered on the cleavage surfaces and on the lateral faces (e.g. in kaolinite), where are respectively the original -O- quickly transformed in -OH groups. The H^+ is exchangeable for a cation and reacts as a week acid. On the cleavage surface -OH is linked on the Al, (e.g. kaolinite) as on the lateral surfaces -OH is linked on the Al or Si ions.

As a remark it must be said that the allophanes have also -OH groups on their surfaces which have the same properties as the exposed -OH groups on the clay minerals.

1.3. The physico-chemical properties of specific primary particles.

1.3.1. Properties of the hydroxydes.

1.3.1.1. $Si(OH)_4$.

First the case of ordinary quartz will be treated. It is composed of tetrahedrons SiO_4 in which each O is sheared by two tetrahedrons. When O is exposed, the following hydrolyses occurs:

$$\begin{array}{ccl} \mathrm{Si - O -} & \vdots & \mathrm{Si} \rightleftarrows 2\ \mathrm{Si - OH} \\ \mathrm{H} & \vdots & \mathrm{OH} \end{array}$$

The $-Si-OH$ is slightly acid, just like silicium acid and consequently it is slightly negative $-Si-O^-$. In soil positive charged silica was never found. To reach this, a pH of about 1-2 is necessary. In other words, the amphoteric character of $Si(OH)_4$ is not known in soil. This is not the case for other sesquioxydes such as formed by Al and Fe. The behaviour of $Al(OH)_3$ is the best known and is also the most important in soils.

As $Fe(OH)_3$ neverbecomes toxic in the soil, the special behavior of iron is used to promote the structurization of sandy particles as will be explained further.

1.3.1.2. $Al(OH)_3$.

In general one may say that in acid conditions the OH^- groups will get associated with H^+ from the environment to form on one hand H_2O and on the other hand $Al(OH)_2^+$, $Al(OH)^{++}$ and Al^{+++} depending on the pH of the suspension. There the rules apply which are known when a weak acid dissociates. In general one can write:

$$ROH \rightleftarrows RO^- + H^+$$

This equilibrium is characterized by the pK value:

$$pH = pK + \log \frac{[RO^-]}{[ROH]}$$

one sees that pH = pK when the weak acid is dissociated for 50 %; indeed, than $[ROH] = [RO^-]$.

Let us take up again the case:

$$> SiOH \rightleftarrows SiO^- + H^+$$

of which pK = 9 - 10. So, a substantial contribution (50 % SiO^-) of the negative charged group is observed when the pH of the soil = 9.

For the dissociation of $Al(OH)_3$ different pK values are known as there are different forms of dissociation as already indicated. For the equilibrium:

$$> Al - OH_2^+ \rightleftarrows Al - OH + H^+$$

the pK = 4 - 5. Consequently, positive charge will be made available in relatively great amounts (50 % being dissociated) starting from this pH value. Such values are well known in soils. The upper limit to get positive charges in any appreciable amount is given by the pK value of the equilibrium:

$$> Al(OH) \rightleftarrows > AlO^- + H^+$$

which is 8 - 9. Consequently starting at such a pH the negative charges on alumina will be of importance.

In summary it might be said that in the pH range normally encountered in the soil, one will find primarily:

$$[Al-OH_2^+]_x \quad \text{and} \quad [Al-OH^{++}]_x$$

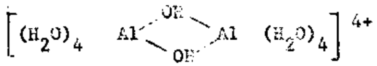
having an appreciable positive charge and at the same time as $Si\,O^-$ having a very weak negative charge.

Small quantities of organic acids such as one may find in the soils are sufficient to liberate appreciable quantities of aluminium from the clay particles specially from the octahedron sheets starting at a pH 5.2 up to 7 (Jackson, 1968). Once hydrated, following equilibrium in function of the pH is established:

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftarrows [Al(H_2O)_5OH]^{++} + H_3O^+$$

Octahedron configuration:

$$2\,[Al(H_2O)_5\,OH]^{++} \rightleftarrows [Al_2(H_2O)_8\,(OH)_2]^{4+} + 2\,H_2O$$



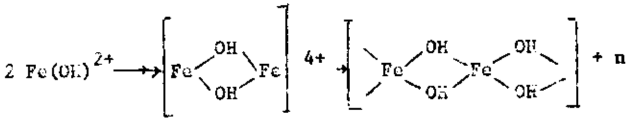
This phenomenon, called protonation (proton being put at the disposal) is at the origin of the acidity of the water molecules fixed at the surface of the clay particles. So the water molecules fixed at the clay surface when air-dry have an acidity which is 10 times bigger than the one of ordinary water (Fripiat, 1968). Taken into account the protonation phenomena on the horizontal surfaces of the clays, one might find positive charges as well as the already discussed negative charges, so aggregation processes between the soil particles become possible. Also one can see that when changing H^+ or OH^- or Al concentration of a suspension, one also changes the charge σ and hence the electro-chemical potential ψ of the particle.

1.3.1.3. $Fe(OH)_3$ and its special behavior in structurization of sandy particles.

The divalent iron sprayed on soil undergoes oxidation and changes into ferric form. A Fe^{3+} ion, having six coordination bonds, is initially bound to six H_2O molecules, which undergoes stepwise hydrolysis. According to Stumm and Morgan (1970), a stepwise hydrolysis can be presented by the following reactions:

$$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5OH^{2+} + H^+ \rightleftharpoons Fe(H_2O)_4OH_2^+ + H^+$$
$$\updownarrows$$
$$\underset{\text{(solid)}}{Fe(OH)_3(H_2O)_3} + H^+$$

In effect, as soon as $Fe(OH)^{2+}$ species are formed, the process of polymerization starts due to their interaction among each other through condensation process. Polymerization can be shown as follows (Dousma and De Bruyn, 1976):



These polymers carry a net positive charge. When precipitated on the surface of quartz grains due to van der Waals attractive forces, they leave a net positive charge on these particles, a phenomenon known as activation of neutral surface. These positive charges on quartz grains can interact with the -C=O functional groups of PAM molecule and improve the adsorption of PAM with respect to its adsorption on sand only treated with PAM.

1.3.1.4. Charge of the colloids.

Through the charge density σ (see p. 4), one understands the quantity of electrons (available or lacking, negative or positive charge per unit surface.

By potential ψ one understands the work needed to bring one unit charge from a large distance where it is not influenced by the charged surface of the clay, to the very charged surface.

When the intermicellar solution contains ions identical to the ions composing the colloids, one says that the solution is an electrolyte determining the electro-chemical potential.

There are other solutions containing no identical ions, which are called indifferent electrolytes, because they cannot change the potential of the particle. This can be explained as follows: ions of opposite charge as the one on the surface will come close to the charged surface, but cannot enter it to discharge the surface due to stereo-chemical obstruction.

Remember it was already pointed out that cristalline colloids have a charge which does not change practically speaking. This means that in such a case the absorbed exchangeable ions (contre-ions) cannot discharge completely the surface when the origin of the charge is to be found in the interior of the tetrahedrons or octahedrons (isomorphic replacement). The surface charges due to broken bonds however, can react differently depending on wether one is dealing with indifferent electrolytes or electrolytes containing the potential determining ion. The different cases are discussed further in the text. They offer a particular interest when one has to discuss the flocculation due to increase in concentration or due to increase the valency of the contre-ions.

1.3.2. Properties of the different kinds of clay minerals.

Montmorillonite is named after a locality in France, Montmorillon. It is an expanding clay mostly consisting of very small flake-shaped units without regular outlines (amorpheus fringes). As known, the unit is composed of two silica tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedrons per sheet point in the same direction and towards the center of the unit. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layers are O; the OH of that layer being located in the midst of the hexagon formed by the tips of the tetrahedrons.

In stacking the units, the bases of the tetrahedron are oriented toward each other so that the O layers of one unit is adjacent to the O layers of the neighbouring unit. This is a first reason for an easy cleavage between two units. A second reason is that the isomorphic replacement happens mainly (for 80 %) in the octahedrons and the remainder in the tetrahedrons.

Consequently, the tetrahedrons have small charges and the affinity to fix cations between two adjacent ones is small. So the adsorption of water molecules between the units, together with the hydration of the cations located there, is easily understood. Montmorillonite is a clay mineral which is formed when the aquous environment is rich in divalent ions, mainly Mg^{2+} and when the drainage of the site is poor.

In the same 2:1 group the mica's should be mentioned. Here the isomorphic replacement is very regular, mainly in the tetrahedral sheet where 1/4 Si^{4+} is replaced by Al^{3+}. So the negative charges are fixed in the silica sheets and consequently the cations are mainly fixed on the surfaces and bottoms of the units, making so the link when particles are staked. The difference in behavior with montmorillonite can be explained concerning the lack of expanding when put in water. Individual mica sheets are rarely observed, but stacking are well known. In pure mica's the link between two subsequent units is made through non-hydrated K^+ ions. Its diameter fits exactly the hexagonal cavity formed by the bases of the six tetrahedrons to the silica sheet. When the particle is altered and the K^+ ion hydrated, which is now more loosely fixed between the units, then one speaks about hydromica's. Besides that, isomorphic replacement of Al^{3+} through Mg^{2+} is known and the excessive negative charge which follows from this, is compensated in the substituting O^{2-} by OH^-. This H^+ is consequently not exchangeable, except as seen before on the surfaces of the cristals when they are the consequence of broken bonds.

Illite, derived from the abbreviation for the State of Illinois, is a representative and most common variety of hydromica's. It has a flake like appearance often polymorph, in which the hexagonal shape is prevalent. It has more distinct fringes than montmorillonite.

Only recently chlorites has been recognized as an important constituent of clay material. Its name is derived from the green color of hydrons silicates which were first described as such. Structurally the chlorites belong to the olioctahedral type of class like mica's and illite, but with varying substitution from about Si_3 Al to Si_2 Al_2 in the tetrahedral sheets and from Mg_5 Al to Mg_4 Al_2 in the octahedral layers. Since the understanding that Al atoms can be fixed also in illite clays through the fact that Al^{+++}

become easily soluble in soil at normal pH when organic matter is present (Jackson, 1960), much more attention is now being paid to this clay mineral together with illite, both of which seem to be very common in the temperature regions of the globe, mainly in sediments of marine lagoon and alluvial origin as well as in glacial deposits.

Kaolinite is formed in soils where the drainage is important as in the humid tropics. According to Millet (1964) the solubility of silica in the soil with normal pH is ± 120 mg SiO_2 per litre, this of quartz is much lower and of Na, K, Ca and Mg salts is much higher. The solubility of Al_2O_3 in soil is only 27 mg/litre. So, in sites where the mono- and divalent ions are leached (low pH) the formation of 2:1 type clays is impossible.

Kaolinite is the name of the clay mineral derived from kaolin which is the rock mass composed of such clay usually white in color. The name kaolin is the wrong phonetics of the Chinese "kauling", meaning high ridge, the name of a hill near Jauchan Fu, China, where the material was obtained centuries ago.

In kaolinite the isomorphic replacement is weak and consequently its base exchange occurs mainly on the edges (broken bonds).

In water kaolinite stackings or lamines separates much easier in individual unit than does montmorillonite and illite (Emerson, 1959). Hence, soils rich in kaolinite will pose severe problems when irrigated. This is explained by the fact that in kaolinite the octahedrons of aluminium exposes on top OH groups which through hydrogen bonds will fix water, loosening in such a way the -OH-O- bonds between the tetrahedral and octahedral sheet when kaolinite particles are piled up in a clay domain or stack (fig. 2).

Sepiolite(1) is long time been considered as synonymous with "Meerschaum", the German word for "sea froth" alluding to the lightness and color of that material. Sepiolite is derived from the Greek "cuttle fish", the bone of which is light and porous. Palygorskite is the name given to a family of fibrous hydrous siliceous clay minerals and attapulgite is named after the fuller's earth found in Attapulgus, Georgia. All three clays have in common their hornblende fibrous like structure, composed of double-chains of silica and in which there is considerable replacement of magnesium by aluminium in the central trioctahedron chain. The formula of attapulgite after Bradley would be:

$$(OH_2)_4\ (OH)_2\ Mg_5\ Si_8\ O_{20},\ 4\ H_2O$$

The special structure is the reason why this clay particle appears as single lath or bundles of laths. The difference between the three types mentioned may be in the degree of the replacement of magnesium by aluminium in the structure.

These clays are frequently found in recent sediments accumulating in dry desert basins. The abundance of magnesium seems to lead to their formation, otherwise they are very soluble in acids and they would be destroyed if solution of the carbonates by acids preceded attempts at clay-mineral identification (Grimm, 1953). Much more than was known up to now, these minerals seem to be very frequent in the large basin area of North Africa, the Near- and Middle East.

It is remarked that most of the exchange positions (as in kaolinite) are at the edges with a relative few on the cleavage surfaces, which are here parallel to the c axis.

Finally, one must remember that many clay materials are composed of more than one clay mineral and that clay minerals may be mixed in several ways. There might be interstratification as well as discrete mixtures of different clay particles. In the first case, it might be regular or random irregular, mixed layers of illite and chlorite are particularly common. Mixed layers cannot be given specific names nor properties; they can only be designated through the layers involved. Mixed layers when stacked or packed can give as stable domains as those composed of a single kind of units.

1.4. The formation of aggregates (clay domains) from primary particles.

The aggregates can be subdivided in micro- and macro-aggregates. The micro-aggregates when consisting only of clay particles are called clay domains. They have a diameter < 250 to 500 microns. The macro-aggregates

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(1) The origin of the names of clay minerals is according to Grim (1953): Clay mineralogy, Mc Graw Hill Co., New York.

have a diameter superior to this, but inferior to 10 mm. The structural elements superior to 10 mm are called clods.

The forces which keep the elementary particles together are:

1. Intermolecular forces (Van der Waals forces; H bonding and protonation)
2. Capillary forces resulting from the existance of a meniscus
3. Chemical forces including the influence of the adsorbed counterions by electrostatic bounding by ion exchange
4. Coordination bonding or ligand exchange

Particles have to be close to one another in order that intermolecular forces might interfere. To bring them close together, they must be first flocculated or coagulated.

1.4.1. The flocculation and coagulation of soil particles.

It must be pointed out that flocculation and coagulation are two different notions. When particles are agglomerated but easily or difficulty dispersed afterwards, one says that they are respectively flocculated or coagulated (see further fig. 4).

A direct flocculation might happen when the particles are less than 1 micron. The micro-aggregates thus obtained do not exceed 250 microns. When the elementary particles are larger than 5 microns, aggregation does not take place directly, but by means of colloidal particles which, if necessary, have been neutralized in advance serving in such a way as a binding between the larger particles.

The particles of the same charge, having sizes ranging from 1 to 5 microns, need neutralisation up to a critical value (the critical charge) before they can get agglomerated. At that moment, the precipitate may have a remainder of electrical charge which is important enough to flocculate other particles making up in such a way, even bigger aggregates as showing in fig. 3.

A flocculation and even a coagulation might occur directly when the particles have a different charge such as clay (-) and hydroxyles (+) of iron of aluminium when present in a suspension of pH 5.5 - 7.

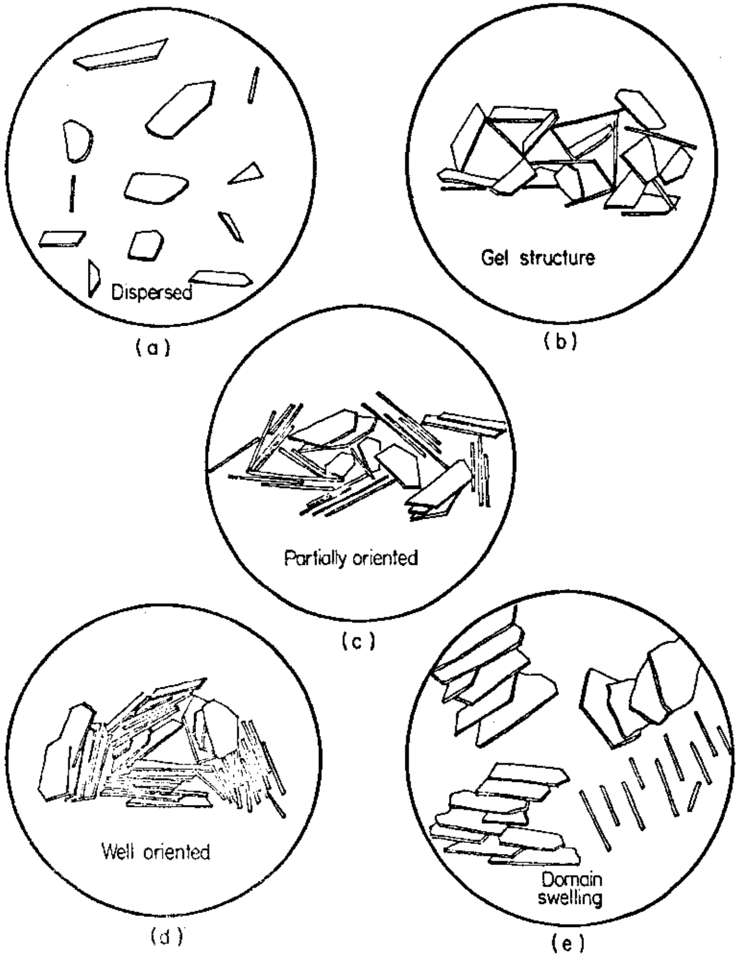

Fig. 3. Clay particle arrangements in disordered, gel-like, structures, and in well oriented domains (43).

The flocculation of particles smaller than 1 micron having the same charge does not pose a major problem, as the smaller the particles, the easier they are assembled by the Brownian movement, and the greater the possible points of contact per unit mass. Under the influence of thermal energy (kT), these small particles will move through the water molecules colliding and finally they will get the same kinetic energy ($1/2\ mv^2$) as the water molecules.

The symbols have the following meaning:

$k = \frac{R}{N}$ R = universal gas constant = 8.3×10^7 erg per °C per mole
N = number of Avogadro = $6.02\ 10^{23}$
T = absolute temperature = 273 at 0 °C
m = mass of a H_2O molecule
v = speed of such a molecule

The greater the specific surface, the greater the total surface energy. Indeed, in order to increase the specific surface, labour has to be done. This is why the alteration fringe mainly on montmorillonite is so important to consider in respect to aggregate stability which is greater than with other clay minerals.

1.4.2. The flocculation of particles having the same charge.

The existence of a charged surface in contact with the liquid phase is the cause of the existence of an electrical double layer in which the orientation, the concentration, the activity and the potential of the ions are different from the ones in the same solution, but being at a remote place from the charged surface. This is charged because of isomorphic replacement, the broken bonds and the amphoteric character of the sesquihydroxydes, which, as was mentioned before, come on the surface as a consequence of broken bonds and cleavage. The concept of the double electrical layer is of major importance for the good understanding of the flocculation of particles having the same charge.

The first substantial theory on the double electrical layer was given in 1879 by Von Helmholtz, who suggested that the double electrical layer was virtually a condensor with two parallel plates of which one was charged positively and the other negatively at an extremely small distance

The surface of the particle has its own charge, mostly negative as is said, forms the inner layer, and the ions in the solution in front of the charged surface is called the contre-ions and they make up the outer layer. This theory was improved a first time by Gouy in 1910, who developed the conception of the diffuse double layer. The outer layer in this case is represented by an atmospheric distribution of the ions facing the charged surface i.e. the ion concentration is more dense in the vicinity of the charged wall than at a given distance (see fig. 4).

Even later, Chapman in 1913, independently announced the same theory. So it comes that nowadays it is called the Gouy-Chapman theory. Stern in 1924, not in agreement with this conception, argued that the outer layer consisted partly of the Helmholtz layer and partly of a double layer, as said by Gouy and Chapman.

The atmospheric contre-ion distribution in the double layer is determined by:

1. Charge density σ on the surface of the colloid
2. Valence of the contre-ions v
3. Total concentration of the electrolyte Co
4. Thermal energy of the ions kT
5. Dielectrical constant ε of the liquid (solvent)

The interaction on the ions of the electrical field forces originated by ψ i.e. the electrical field characterised by ψ when taking into account the distance and kT, one may expect that the distribution of the ions facing the charged surface will not be linear but logarithmic. So, one has found out that the ion distribution of the outer layer is described by the Maxwell Boltzmann formula:

$$C = Co\ e^{\left(\frac{V\ e\ \psi}{kT}\right)} \qquad (1)$$

where: C = ionic concentration of the electrolyte at a given distance x from the charged surface
Co = ionic concentration of the electrolyte at a remote distance from the charged surface so that the electrical field force emanated from this surface is no longer of influence on the ions there
e = charge of the electron = 4.8×10^{-10} electrostatic units
$\psi = \psi_x - \psi_r$ = difference in potential obtained by the ion being at the distance x where one wents to know C. The ions of Co having the reference potential ψ_r

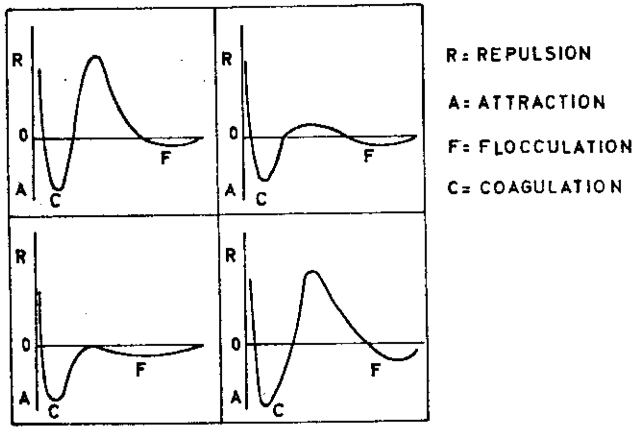

FIG. 4. DIFFERENTS DEGREE DE FLOCCULATION ET DE COAGULATION

Different degrees of flocculation and coagulation

In order to know the value of ψ at a given point, one has to know its dependence on the charge density at that point(ρ). One has found that the distribution of ψ in the outer layer is given by the formula of Poisson, deliberately admitting that the charged surface is plane and infinite.

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{\varepsilon} \tag{2}$$

where $\frac{d^2\psi}{dx^2}$ being the change in the intensity of the electrical field $-\frac{d\psi}{dx}$ in function of the distance x and ε, the dielectrical constant of the solvent

It is pointed out that C and ρ in (1) and (2) have the same meaning, i.e. the ionic charge concentration per cm^3. Formula (2) tells that ψ diminishes more rapidly than linear in function of x. So, in fig. 5 and 6 it can be seen that when all other things stay equal, that C as well as ψ increase when approaching the charged surface, but at a different rate. One can understand why C increases more rapidly than ψ. The latter being given by the product of the force times the distance. The force emanating from an indefinite charged surface is in first approximation constant and is given by the charge density. The distance is given by the thickness of the double layer. When C is doubled, so will be the force, but as will be seen later on, the thickness of the double layer will get smaller. Hence the distance and consequently ψ is not doubled.

The main problem now is to find a solution satisfying (1) and (2) for the boundary limits characterising the colloids in the soil. This is extremely difficult and one may even say that a general and satisfactory solution for all aspects is not yet found. Nevertheless, it is possible to study approximation when C is small. The solution in such a case can be:

$$C = \left(2\ Co\ \varepsilon \frac{kT}{\pi}\right)^{1/2} \sinh 1/2 \left(\frac{Ve\psi}{kT}\right) \tag{3}$$

1.4.3. <u>The thickness of the double layer (δ).</u>

In order that this formula might have a direct significance, two parameters have been introduced, δ and κ.

$$\delta = \frac{1}{\kappa} \quad \text{and} \quad = 8\pi \left(\frac{C^2V^2}{\varepsilon kT}\right)^{1/2}$$

This is necessary as the double diffuse layer does not have well defined limits.

By δ one understands the "thickness" of the double layer. δ is defined as the distance over which ψ diminishes $\frac{1}{e}$ of its initial value on the charged surface, ψ_o; e being the base of the natural logarithm = 2.7183 and $\frac{1}{e} = 0.37$ (see fig. 6).

As was pointed out that clays have a constant charge and that ordinary colloids have a constant potential when the electrolyte contains only indifferent ions, one can study the change of C when x becomes smaller taking into account formula (3).

a. Concerning the colloids having a constant ψ_o. One can see from (3) that C is proportional to $\sqrt{Co}$; as an increasing Co the ions are more attracted to the charged surface δ diminishes. In order to keep ψ_o constant C must increase and so will ψ (see fig. 5).

b. Concerning the colloids having a constant σ. In (3) one can see that ψ is inversely proportionel to $\sqrt{Co}$; so when increasing Co, ψ_o will diminish quite rapidly. When calculating δ at a temperature of 20 °C one finds:

$$\delta = \frac{3 \times 10^{-8}}{v \sqrt{M}} \qquad (4)$$

M = molarity of the electrolyte.

Formula (4) enables us to make practical conclusions as can be seen from the following examples:

(A 0.1 N NaCl solution has a $\delta = \frac{3 \times 10^{-8}}{1 \sqrt{0.1}} = \frac{3 \times 10^{-8}}{0.32} = 10^{-7}$ cm = 10 Å

When diluting 100 times one gets a solution of 0.001 N; δ = 100 Å

(A 0.1 N $MgSO_4$ solution has a

$$\delta = \frac{3 \times 10^{-8}}{2 \times 0.32} = 5 \text{ Å}$$

When diluted 100 times, one gets δ = 50 Å.

Formula (4) learns about the influence of the valencies of the ions and of their concentration on δ.

1.6. Summary.

When an electrolyte is added to a clay colloidal suspension, it can be said that:

1. There is an exchange of the ions present on the solution side of the fixed liquid coat of the double layer for those of the same sign added with the electrolyte. If the added ions are more strongly adsorbed than those which are displaced, the thickness of the double layer will be decreased; consequently the ζ potential will be lowered and flocculation occurs (whereas those ions which produce a high potential will cause dispersion).
2. The free energy of the water is lowered (this is also so when adding ethylalcohol) in the bulk of the solution and water moves from the regions of the double layer into the solution, because of the free energy gradient established. The result is a contraction of the double layer lowering also the ζ potential. The amount of electrolytes to be added depends on the original ζ potential of the system. It is obvious that the addition of a large amount of an electrolyte causes always flocculation.
3. Every collision between particles procedures adhesion as soon as the ζ potential is lowered to or below the critical value; this is the case of a rapid flocculation. When two particles approach sufficiently close, the Van der Waals' attractive forces cause them to stick together. These forces are proportional to $1/r^6$ and are consequently active only at very close range. If the particles are similarly charged, work has to be done

in bringing up one through the electrostatic (Coulomb) repulsion of the other. The repulsive force is proportional to $1/r^2$ and hence is active at relatively long range. This force hinders the approach of the particles to the critical distance at which they stick together.

If the potential is higher than the critical ζ potential, some flocculation may still occur, for the momentum of the faster moving particles can carry them through the repulsive electrostatic fields within the range of the Van der Waals' attractive forces. This will be mainly the case with very small particles.

1.7. Practical application.

In agricultural practice one sees that aggregate stability is increased by adding Ca-ions and Fe-ions to the soil. Since more than 1000 years (Tiulin, 1928) it is known that liming is a good method to improve soil structure. The increase in water stability of the aggregates by saturating the clay with calcium has been proved several times.

Recently the addition of Fe-ions was also introduced in pratice, e.g. the use of Floral (ferriamonium alum) to improve structure deteriorated soils.

The easy dispersion of sodium saturated clay in newly reclaimed polder soils and in semi-desert soils is explained by the large waterhull around the sodium-ion. Consequently the salt content of irrigation water is to watched very carefully. The reclamation of these soils can be carried out by applying a great quantity of calcium sulphate. When the infiltration and the drainage of the land is good and sufficient amounts of water are available, then the calcium ion entering the soil will replace the sodium and the chlorine is moved together with the excess of calcium to form a very soluble produce being $CaCl_2$ (59.5 g soluble in 100 ml H_2O). The other produce which is formed is Na_2SO_4 which is also very soluble (46.8 g per 100 ml H_2O).

However, if one wants to reclaim saline soils, the osmotic pressure of the sodium fixed on the clay particles, is the reason why the macro- or the micro-aggregate pores diminish in size and diminish in such a way the permeability and infiltration rate. So, even when gypsum is put on the soil and irrigation water is allowed to flow over it, the water cannot penetrate and hence the calcium cannot replace the sodium. In order to be successful in reclaiming such soils, one is bound to stabilize first the aggregates which one can make mechanically by working the soil at the right moisture content. This stabilization can be done using artificial products such as bituminous emulsions. After fine grinded gypsum (5 - 10,000 kg/ha) is put on the soil,then one may irrigate. In such conditions the calcium ion can penetrate into the soil and replace the sodium ion.

Another feature from pratice to be explained is the high stability of acid soils, this stability is not only due to the H^+ ion adsorption, but also to the strong flocculation value of Al^{+++} ions which became available in acid clay soils. In general, however, the aggregation in acid soils is less stable than in calcium saturated soils, one of the reason is that in acid soils the organic matter does not have the sticking property, which is a characteristic of Ca saturated organic matter.

To get a better idea of the soil components which are active in the formation of stable aggregates, Kolaskova and Akberdina (1959) examined aggregates of different sizes from the Volga-Kam wooded steppe. They found that the aggregates smaller than 0.25 mm, the so-called micro-aggregates, contained more clay, humus, mobile acids, SiO_2, R_2O_3, P_2O_5 and mobile Fe than the larger aggregates.

These results, however, could not be confirmed in the study of Antipov-Karataev and Kellerman (1962) who compared aggregates from tschernosems, podsolic, gray-wooded and red loamy (Krasnosem) soils. It is believed that part of the explanation why there is a difference in composition in some but not in all soils between the stable and unstable aggregates, may be found in the fact that it will depend on the genesis of the soil profile, whether or not this difference will exist. Indeed, the degree of illuviation per horizon can be responsible for the composition of the colloidal material of the studied soil.

1.8. The genesis of the macro-aggregates.

The following phenomena are involved in the formation of the macro-aggregates:

1. The chemical stabilization or cementation,
2. The drying out effect which gives rise to capillary forces,

3. The bonds made a colloidal substance between coarse particles and/or micro-aggregates. Herein are also included the adhesion forces between mineral particles and organic matter such as humus, krilium, gelatine, polyuronides, bitumen, polyvinylalcohol, polyvinylacetate,
4. The tension and pressure exerted mechanically on the soil so that locally sites having greater density will occur, which, afterwards, will form the clods when the soil is broken up again.

1.8.1. The chemical stabilization of the aggregation.

In soil survey one knows that aggregates in soil periodically suffering from an excess of water are more stable than the normal calcium-saturated aggregates in well-drained profiles. The explanation is that during periods of water excess, through the reduction processes in the soil profile, an amount of soluble bivalent iron ions is liberated which can penetrate the aggregates. During the drier period, when the water table goes down, through oxidation the Fe^{++} changes into Fe^{+++} and is precipitated as colloidal $Fe(OH)_3$, which cements the aggregates. Dehydration and crystallization of the cementing $Fe(OH)_3$ may be the origin of very hard iron concretions or even iron pans. Not only iron, but also calcium, manganese and phosphorus may be important as chemical stabilizers of aggregates, when they are changing the soluble into the insoluble state (carbonates, oxides, phosphates).

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2\nearrow + H_2O$$

$$CaCO_3 + 6\ H_2O \rightleftarrows CaCO_3 \cdot 6\ H_2O$$

$$CaH_4\ (PO_4)_2 + Ca(OH)_2 \rightleftarrows Ca_2H_2\ (PO_4)_2 + 2\ H_2O$$

$$Ca_2H_2\ (PO_4)_2 + Ca(OH)_2 \rightleftarrows Ca_3\ (PO_4)_2 + 2\ H_2O$$

The concept of cementation is reserved for the phenomenon where products which are altered chemically enhance the hardening of the soil structure as a whole.

1.8.2. Formation of soil crumbs by dessication.

Dessication brings the colloidal soil particles closer together. When the electric forces, following the law of Coulomb are inversely proportional to the second power of the distance, the Van der Waals' forces, however, are inversely proportional to the sixth power of this distance. In crumb formation the role of water is really important, because when the amount of water diminishes the curvature (1/r) of the water meniscus between two soil particles will increase and hence will bring them closer together. This might be so important that the Van der Waals' forces become predominant on the Coulomb forces.

In a dry and dusty soil the air surrounding the elementary soil particles prevents them from coming close together, so that no intermoleculary attractive forces originate. The moistening of such soil causes the formation of a water hull around the particles; this way the small altered amorphous coat of the mineral particles swells and simultaneously a meniscus is formed between the particles. The force p of the meniscus (interfacial curvature) to keep particles together may be put equal to the capillary tension, for which the equation of the height of capillary rise is valid(1):

$$h = - p = \frac{2T\ \cos\theta}{r\ d\ g} \qquad (7)$$

where h = height of capillary rise in cm
P = force in dynes/cm^2
r = radius of the pores in cm
T = surface tension of the water (72 dynes per cm)
θ = angle of contact between water and soil (angle = 0; cos θ = 1)
d = density of water in g/cm^3
g = acceleration of gravity (981 cm/sec^2)

There exists a moisture content by which the cohesion among the particles is maximum. This water content is called the critical moisture content for soil structure formation. Roughly it is estimated to be 60 to 90 % of the field capacity. It can be measured in the laboratory by subjecting a given volume of soil at a different moisture content to 1000 standardized knocks (see fig. 5). The moisture content at which the volume of soil remains the highest is the critical value (see fig. 6 a, b, c).

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(1) Equation of the capillary rise, also known as "Law of Kelvin (in Anglo-American publications), as "law of Bechold" (in German studies), or as "law of Jurin" (in French publications).

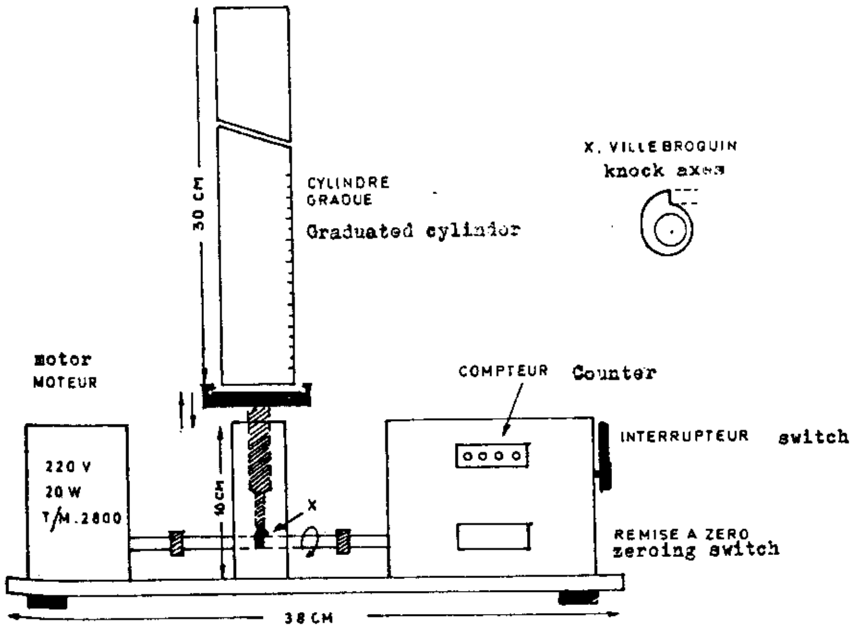
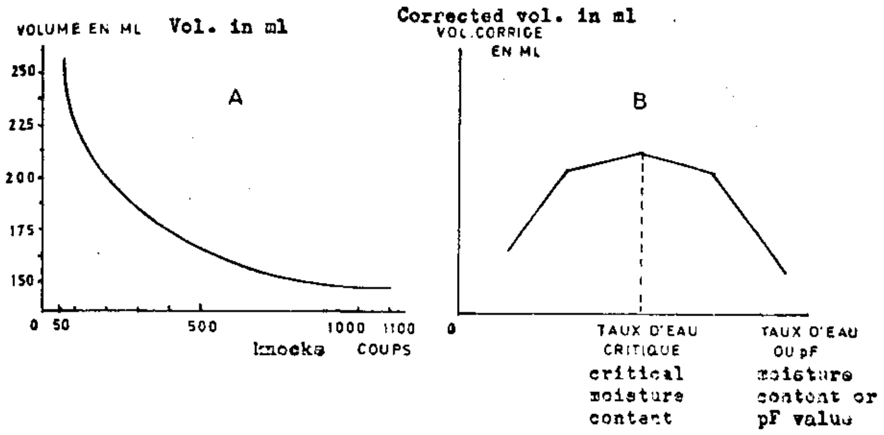


FIG. 5. APPAREIL POUR DETERMINER LE TAUX D'EAU CRITIQUE DE FORMATION DE STRUCTURE

- Apparatus for determining the critical moisture content for aggregate

FIG 6.



APPAREIL DE COMPACTAGE

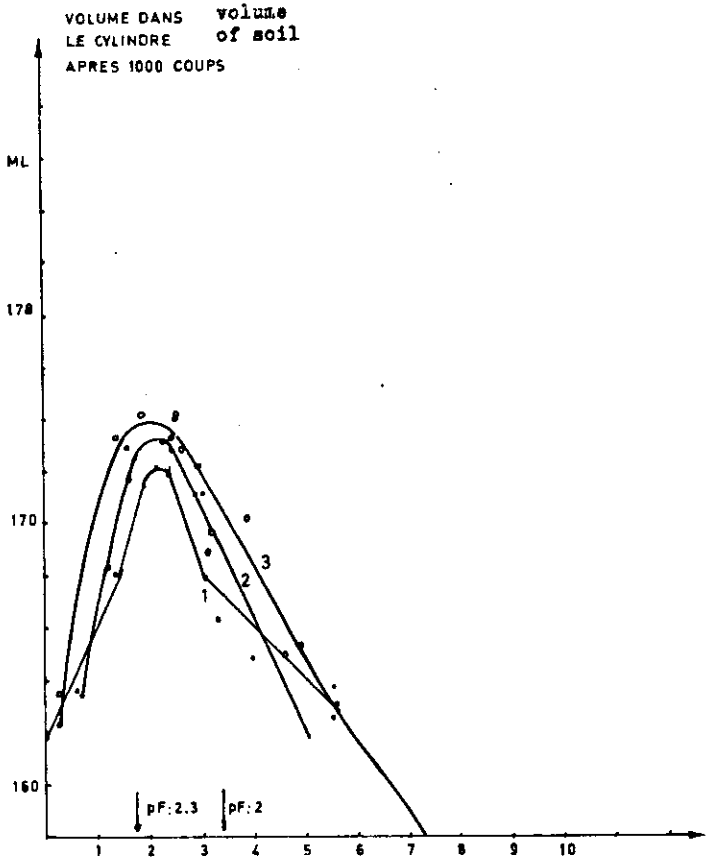


FIG 6'C. ESSAI DE COMPACTAGE POUR CONNAITRE LE TAUX EN EAU CRITIQUE DES SABLES DE BEERVELDE

1.2.3 NOMBRE DE REPETITIONS ESPACES DANS LE TEMPS

Compaction trial to know the critical moisture content on sands from Beervelde
1.2.3.=number of repetitions

The reason for the existence of such a moisture content is that it is the resultatut of two opposite forces, the capillary force due to the presence of the meniscus and the disjoining pressure due to the presence of the electrical charge of the same sign between the particles. The first one is attraction force and is proportional to $1/r$; the second one is repulsive and proportional to $1/r^2$ (see fig. 11). So when the moisture content increases the meniscus will get more flat and the particles can fall apart; when it gets drier, then the disjoining pressure is increased and the cohesion among the particles will get lower. This can be demonstrated very sharply in sandy soils (see fig. 13 a, b, c). In loam and clay soils, the Van der Waals' forces might get involved also. These will be greater, the greater the possibilities of contact among the particles. This is the function of the alteration zone around the individual clay minerals and the degree of moistening. The aggregate will be the more stable when dried, the wetter they were when the soil samples were taken. Also when the clay composition is different, a montmorillonite will be more stable than a kaolinite.

It must be pointed out that keeping the particles together is due to moisture tension. When the different critical moisture contents are compared with the tension, for sandy soils they are equal to ± 200 cm tension and for clay soils with ± 500 cm. The water film around the particles at those tensions are respectively, according to formula (7), 7.5 μ and ± 3 μ.

Schofield remarked in 1954, that also in clay domains there is a critical distance between the clay particles giving rise to a maximal stability. This should be ± 9 Å, being the size of about 3 water moecules. This equilibrium should be due to a balancing unit of the Van der Waals' forces and the repulsive forces due to the Born repulsion (roughness of the surfaces of the clay minerals and the presence of water layers which are hard to remove).

A summary of the different cases is given in fig. 4.

1.8.3. The bonds between the mineral particles.

When dry clods are put in contact with water, one sees that the aggregates explose due to compressed air trapped at the interior, as water entering nearly simultaneously all the capillaries. This phenomenon

is called slaking or desaggregation. This is a distinct feature from dispersion. The latter is due to lack of coagulation or flocculation of the individual clay particles. When slaking, the particles will stay together in a clay domain, when dispersing, the individual particles are no longer in close packing, but are removed from one another. Slaking can be seen distinctly from dispersion, when a clod is put in a water-alcohol mixture. Through the trapped air, the clod will slake, but through the alcohol, the colloidal particles will be flocculated and stay in a clay domain. Dispersion of a clay domain will be observed when adding more water to the system. Dispersion can be prevented by increasing the organic matter content. The latter has been water repellent properties and so it prevents the water from entering all capillaries quickly.

A model after Emerson (1959) of an aggregate is given in fig. 7 and 8, depending on whether or not the amount of clay is small or large (20 %). In the first case, the clay bond is made up of one clay domain, as in the second, more than one clay stack is necessary to link the sand particles together.

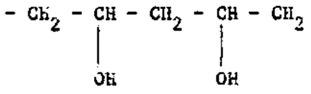
The reason why aggregates might have a difference in stability is the difference in bonds between the particles. Four cases can be distinguished

a. intergranular bonds due to the water meniscus giving rise to poor stability, only at the critical moisture content the stability will be reasonable good

b. intergranular bonds due to natural products such as humus or flocculated clay or artificial non-ionized or weakly ionized polymers such as polyvinylalcohol and polyvinylacetate, depending on the case, the structure is medium or stable.

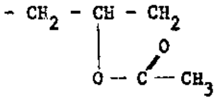
c. peripherical bonds made up from chalk, cement, bituminous micels, ionized polymers having carboxylic sulfonic, amidic or aminic groups present:

Examples of the mentioned polymers are:



$$- CH_2 - \underset{OH}{\underset{|}{CH}} - CH_2 - \underset{OH}{\underset{|}{CH}} - CH_2$$

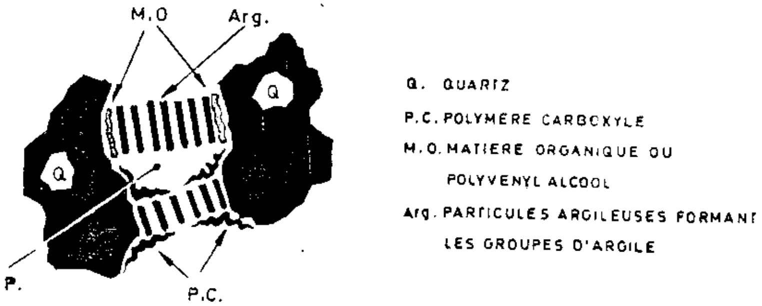
polyvinylalcohol



$$- CH_2 - \underset{O - \overset{O}{\overset{/\!/}{C}} - CH_3}{\underset{|}{CH}} - CH_2$$

polyvinylacetate

FIG. 7 VUE MACROSCOPIQUE D'UN AGREGAT AYANT SA STABILITE DUE A LA MATIERE ORGANIQUE OU A DES PRODUITS ARTIFICIELS.



Macroscopic view of an aggregate of witch the binding is due toorganic matter or artificial products

Q= Quartz
P.C.= Carboxyl polymere
M.O.= organic matter or polyvinyl alcohol
Arg.=Clay particles grouped into a clay domain

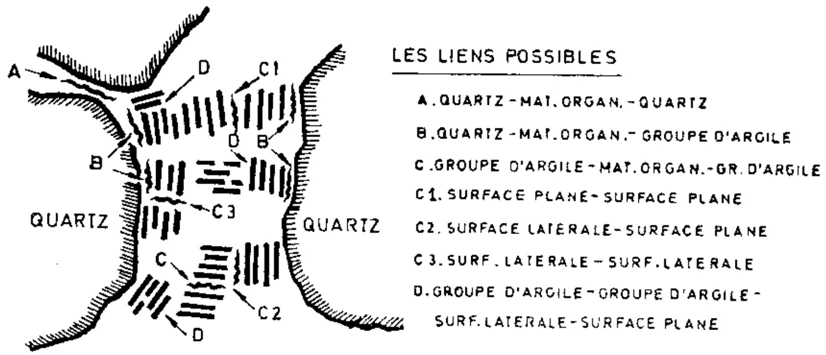


FIG. 8 LES LIENS POSSIBLES ENTRE LES GROUPES D'ARGILE, LA MATIERE ORGANIQUE ET LES GRAINS DE SABLE DANS UN AGREGRAT

Possible bonds between clay domains, organic matter and sand particles in an aggregat

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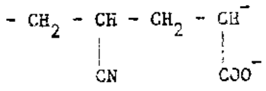
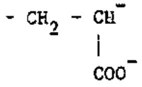


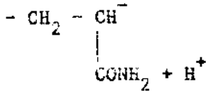
$$-CH_2-\underset{CN}{CH}-CH_2-\underset{COO^-}{CH^-}$$

polyacrylnitril partially or



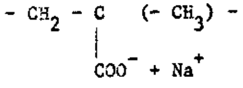
$$-CH_2-\underset{COO^-}{CH^-}$$

completely hydrolysed (krilium)



$$-CH_2-\underset{CONH_2\ +\ H^+}{CH^-}$$

polyacrylamide



$$-CH_2-\underset{COO^-\ +\ Na^+}{C}(-CH_3)-$$

sodium salt of polymetacrylate

d. simultaneously intergranular and perpherical bonds may occur: the combination of the cases b and c when clay content is high (fig. 13) give rise to stable aggregates.

Due to pressure of all kinds (osmotic pressure, soil management, root growth, dessication etc...), the clay particles can get oriented perpendicularly to the direction of the pressure. As the bonds between the particles are the weak points in the aggregates, the breaking up of the aggregates will occur there, and the structural stability is altered. The wetter the soil, the more easy will be the reorientation of the particles, as the binding forces, due to the meniscus get lower. So, it is quite understandable how the heavy machines degenerate the structure when the soil is wet.

Normally there is enough electrolyte in the soil to flocculate the clay. Exception on this rule is made by sodium montmorillonite clay.

When the clay particles are well flocculated, the clay domains, as shown in fig. 8, will stay stable in water. In such a case they are in a metastable situation. This condition is not known in sodium saturated clay and particularly not in sodium montmorillonite. Flocculated montmorillonite by Ca^{++}, Fe^{+++} or Al^{+++} will not disperse in water. The clay particles can be found together to a clay domain when the moisture content is lowered to air dryness. A suction, equal to 14 atmosphere is sometimes sufficient. Under irrigation, when the clay is composed of the 1:1 and 2:1 types, such as kaolinite and illite, the clay particles can get dissociated and the negatively charged horizontal surfaces of illite will get oriented and bound with the positively charged lateral surfaces of the kaolinite. This may happen with individual 1:1 and 2:1 types, such as kaolinite and illite, the clay particles can get dissociated and the negatively charged horizontal surfaces of illite will get oriented and bound with the positively charged lateral surfaces of the kaolinite. This may happen with with individual 1:1 and 2:1 clays, as well as with groups from either type (Schofield, 1954). A special remark is to be made when irrigated soil is composed of kaolinite clays, as it is often the case in tropical soils. The originally flocculated kaolinite clay domains will not stay stable when submerged for a long time. The above named metastable condition exists only shortly. So, quick laboratory tests may give the impression that one is dealing with stable aggregates, but once under irrigation, the clay will disperse progressively. The exceptional behavior of kaolinite domains can be explained by the difference in charge density on the lateral and horizontal faces of this kind of clay. Other clay domains must be shaken or treated mechanically before they disperse.

Once clay particles dispersed, one needs a concentration of Ca^{++} of at least 0.01 M. Expressed in $CaCl_2$ it means that at least one needs 1.11 g per litre. The chalk in the soil is often present as $CaCO_3 . 6 H_2O$. When determined in the laboratory with a HCl test, then often the quantity found is interpreted to be $CaCO_3$. The latter has a solubility of 14 mg/litre at 25 °C, while the solubility of the first named is nihil. In order to know the amount of active Ca^{++} in the soil, the sample must be percolated using NH_4Ac 1N pH = 8 and in the percolate one titrate the Ca^{++} ions using a "complexon" such as E.D.T.A. (ethylene - diamine - tetra acetate).

1.6.4. Interaction organic matter - mineralogical components.

The way the organic links are made to the mineral particles is given in fig. 7 en 8. The discussion on aggregate stability was made as if inorganic matter did not exist. In fact, its influence is considerable on aggregate stability as was mentioned.

Also it can be pointed out that organic matter can eliminate dispersion. Humus is a complex ion which is directly absorbed at the mineralogical parts and lowers considerably the potential of the clay particles. Through the interference of the protonisation at the surface of the clay minerals, due to the presence of Al^{3+} and Ca^{2+}, the negatively charged humus can be fixed (specially the COO^- and SO_3^- groups). On the lateral side of the clay partciles, the exposed Al^{3+}, together with the hydration in the octaeder layer, has also a positive charge at the pH values found in the soil (5 - 7.2) and can also fix the negative groups of the organic matter. On the horizontal surface (001) of the clays, the negative charges may fix the positive charges of the humus, such as the amines ($-NH_2$) and amides ($-CO - NH_2$). So the organic matter is at least ficed in two different ways to the clay particles, as shown in fig. 19. To realize this, the humus has to be elongated and coiled over the clay particles with oriented water molecules in between. As this is the opposite from what happens normally in nature (the increase in free space of molecules being called entropy), it is said that organic matter is fixed through negative entropy.

When looking at fig. 7-8 , it can be understood why aggregates always give the same type of pF curve, independently if they are stabilized through natural or artificial means. The only difference might come from the hydrophylic or hydrophobic properties of the material used. This will be the reason for a quicker or a slower wetting of the aggregates, respectively.

In order to find out what kind of bonds, intergranular or peripherical ones are responsible for the stability of the aggregate, a test can be made using a peptising agent, such as sodium pyrophosphate. The intergranular links will not vanish, but the other will do. This is explained by the fact that only links based on hydrogen bonds will be broken.

When the intergranular bonds are still present, the following distinction can be made: when a soil is treated with an alcaline solution (pH > 10) the non-ionized polymers will stay, but those with amino groups such as humus and gelatine will vanish. This is because the pK value of the amino group is about 9. When soil from an old pasture land is taken and treated with sodium pyrophosphate, no noticeable dispersion will occur. This indicates that the majority of the links are not due to hydrogen bonds. When afterwards, the soil is put in a strong NaOH solution, the aggregates will slake. This indicated that electro-statical links are at the origin of the structural stability.

Using analogous tests, one can find out the difference between bonds, due to ionized and non-ionized polymers.

In agriculture, it is know that incorporation of organic matter into the soil increases aggregate stability (see fig. 9) after Feedkamp. This increase in stability is only proportional to the quantity

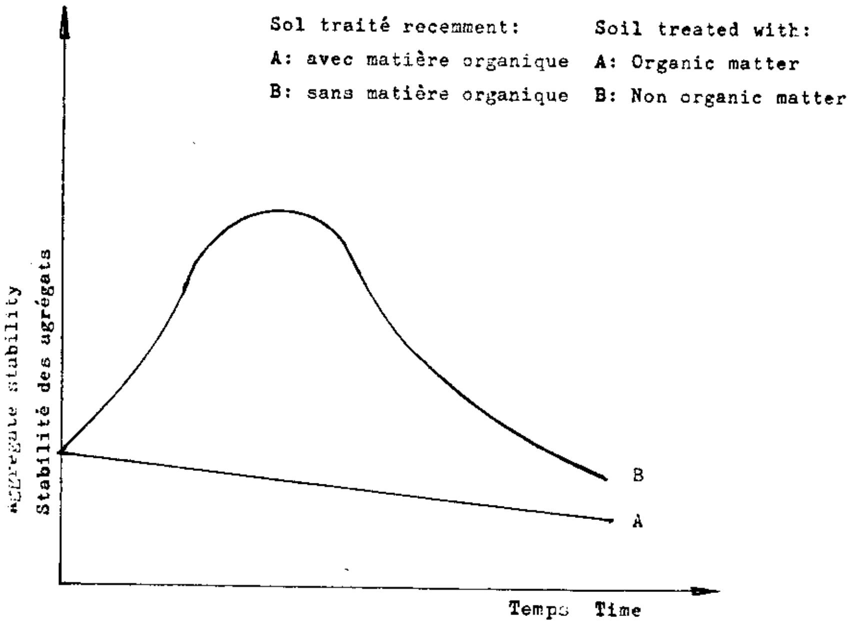


Fig. 9. Evolution de la stabilité structurale dans des terres traitées ou non traitées avec la matière organique.

Evolution of the stability of aggregates in soil treated with and without organic matter

of humus incorporated as long as the overall organic matter level is low. So it was found for the temperature regions, that above 6 %, it does not make such sense to try to increase the organic matter level. In order to have stable aggregates, De Boodt (1948) found that in West-Europe the humus content must be 10 % of the overall clay content (0-2 µ fraction) in the soil. It is evident that at the same time the clay must be flocculated. This finding is based on the fact that when the humus content is determined through wet oxydation by potassium bichromate (Springer and Klee, 1954), it has a C.E.C. of about 400 milliequivalent per 100 g, while illite clay has 40.

In order to study the significance of organic matter in arid and semi-arid (red-brown soils), Greenland, Lindström and Quirk (1962) treated either the soil with periodate ($NaIO_4$) or with NaCl solution. The first one being an oxydant, it destroys the polysaccharides and polyuronides, which is found in places where the microbiological activity is the most important, e.a. in the rhizosphere. The humus which contains $-NH_2$, $-CONH_2$, $-COO^-$, $-SO_3^-$ groups, however, will not be destroyed.

The NaCl is at the origin of the dispersion of clays, although its power is lower than this from sodium pyrophosphate. So, when soil from old pasture land on rendzina or on red podsolic soils are treated with either one of the liquids mentioned, no slaking will occur. However, arable soil with high microbiological activity will slake in $NaIO_4$, but not in NaCl solution. However, when aggregates are well dried out from dry summer and they are put slowly in either one of the liquids, they will stay stable.

For the moment, putting the soil in a good physical condition is booming. Different polymers can be used. In order to be successful, the following steps must be observed:

1. fine powdered gypsum is uniformally put on the soil (5-10 tons/ha)
2. a. mechanical aggregation is obtained by working the soil at the critical moisture content of soil structure formation
3. the obtained aggregation is stabilized using one of the polymers cited above
4. plants having a strong root development are cultivated in order to bring the mechanical structure into a biological stable structure.

The choice of the polymers has to be done in the laboratory where the optimal moisture content, together with the optimal dilution of the polymers can be found out. The combination which gives the highest aggregate stability together with a good pore-size distribution as determined from the pF-curve, will be choosen to be used in the field.