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Clay Properties

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1. Introduction

Most estuaries and several reaches of shorelines have cohesive sediment beds, consisting primarily of clay, fine silt and varying quantities of organic mater. A mixture of that kind is usually called mud. The properties of such a bed are quite different from a sand or gravel bed. The particle sizes, for instance, are less then about 53 μm and the mud has some cohesive properties.

The beds are often formed by deposition of initially suspended sediment. The suspended particles may be flocculated and they tend to settle with a certain settling velocity. The settling characteristics are strongly dependent on the floc size, the suspended sediment concentration and the turbulence intensity, for instance. If several flocs have reached the bottom, a stationary suspension with practically no mechanical strength is formed. Due to consolidation and associated physico-chemical changes of this deposit, a settled bed results with a relatively high shear strength and a stable structural configuration [9].

At this moment the cohesive properties of mud are not fully understood yet. However, from a hydraulics engineering point of view it is necessary to quantify these properties. One may think of the erosion and sedimentation rates in estuarial navigation channels, waterways and harbours, for instance.

Consequently a lot of research has been done to increase the knowledge of the properties of mud. One of the most interesting features of mud is its cohesive property, which is mainly dominated by the clay particles present and arises primarily from electro-chemical forces in the clay-water medium. In the physico-chemistry these forces have been studied extensively, not only for clay minerals and waterbased electrolytes but for colloidal dispersions in general.

A colloidal dispersion is defined as a system in which particles of colloidal dimensions (i.e., roughly between 1 nm and 1 μm in at least one direction) are dispersed in a continuous phase of a different composition. The term colloid is coined from the Greek "κωλλα" and means glue.

In this report an overview will be given of the basic properties of (suspended) clay particles. In section 2 the structure of clay minerals will be described. The forces between suspended particles (section 3) and the possible consequences of them, flocculation or deflocculation (sections 4 and 5) will be discussed next. Section 7 will deal with the mechanism of peptization. Furthermore, some properties of specific clay minerals will be discussed in section 8 and finally some general conclusions will be drawn in section 9.

2. Clay minerals

Clay particles in general have a platelike shape and a layered structure. They consist of a stack of two types of so-called sheets, namely the silicon-oxygen sheet and the aluminium - or magnesium-oxygen-hydroxyl sheet. Less frequent atoms which occur in the latter sheet are: Fe, Mn, Ti, Ni, Cr and Li [10,11].

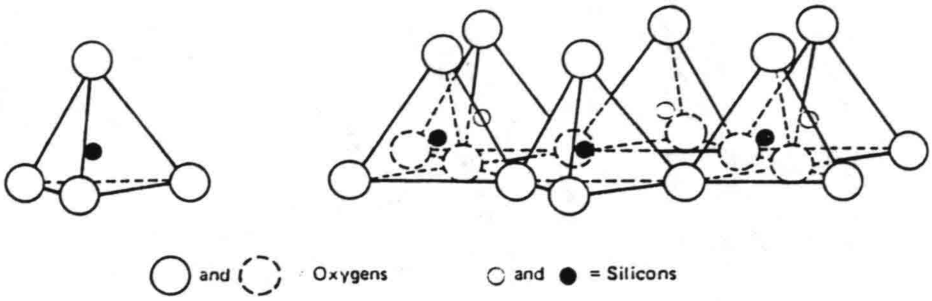

Figure 2.1 Silica tetrahedron and silica tetrahedra arranged in a hexagonal network [10].

The silicon-oxygen sheet is formed by SiO_4 tetrahedra. In such a tetrahedron the silicon atom is equidistant from four oxygen atoms. Three of the four oxygen atoms of each tetrahedron are shared by three neighbouring tetrahedra, forming the silicon-oxygen sheet, also called silica sheet. Projections of this arrangement are shown in figure 2.1. The thickness of the silicon-oxygen sheet is 4.63 Å (1Å = 10^{-10} m) in clay.

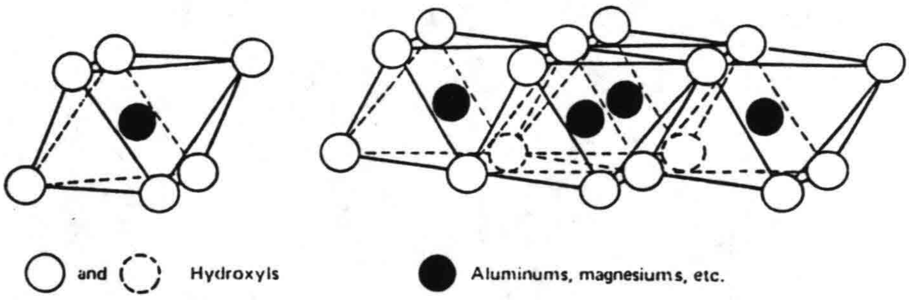

Figure 2.2 Octahedral unit and sheet structure of octahedral units [10].

In the Al- and Mg-O-O-H sheets, the Al or Mg atoms are surrounded by six oxygen atoms or OH groups forming a regular octahedron. The sharing of oxygen atoms by neighbouring octahedra leads to the octahedral sheet. The oxygen atoms and hydroxyl groups lie in two parallel planes with Al or Mg atoms between the planes. This sheet is usually called the octahedral sheet or the alumina or magnesia sheet, also called respectively gibbsite sheet or brucite sheet. An outline of the structure of the octahedral sheet is shown in figure 2.2. The thickness of this sheet is 5.05 Å in clay.

The almost identical dimensions and symmetry allow sharing of the fourth, protruding oxygen atom of the tetrahedral sheet by the octahedral sheet. In the so-called 1:1 layer minerals, atoms are shared between one silica and one alumina sheet, like in kaolinite. There are also 2:1 layer minerals in which one alumina or magnesia sheet shares oxygen atoms with two silica sheets, one on each side like in montmorillonite and illite.

An octahedral sheet combined with one or two tetrahedral sheets is called a layer and most clay minerals are built up as stacks of such layers.

It can be shown that there is a unit cell within each layer that repeats itself in a lateral direction [11]. The arrangement of the atoms in such a unit cell is schematically shown in figure 2.3 for a 1:1 layer clay and a 2:1 layer clay. In this figure the positive and negative valences are presented too. As can be seen, the valences are completely saturated in a unit cell, which means that the unit cell as a whole is electroneutral.

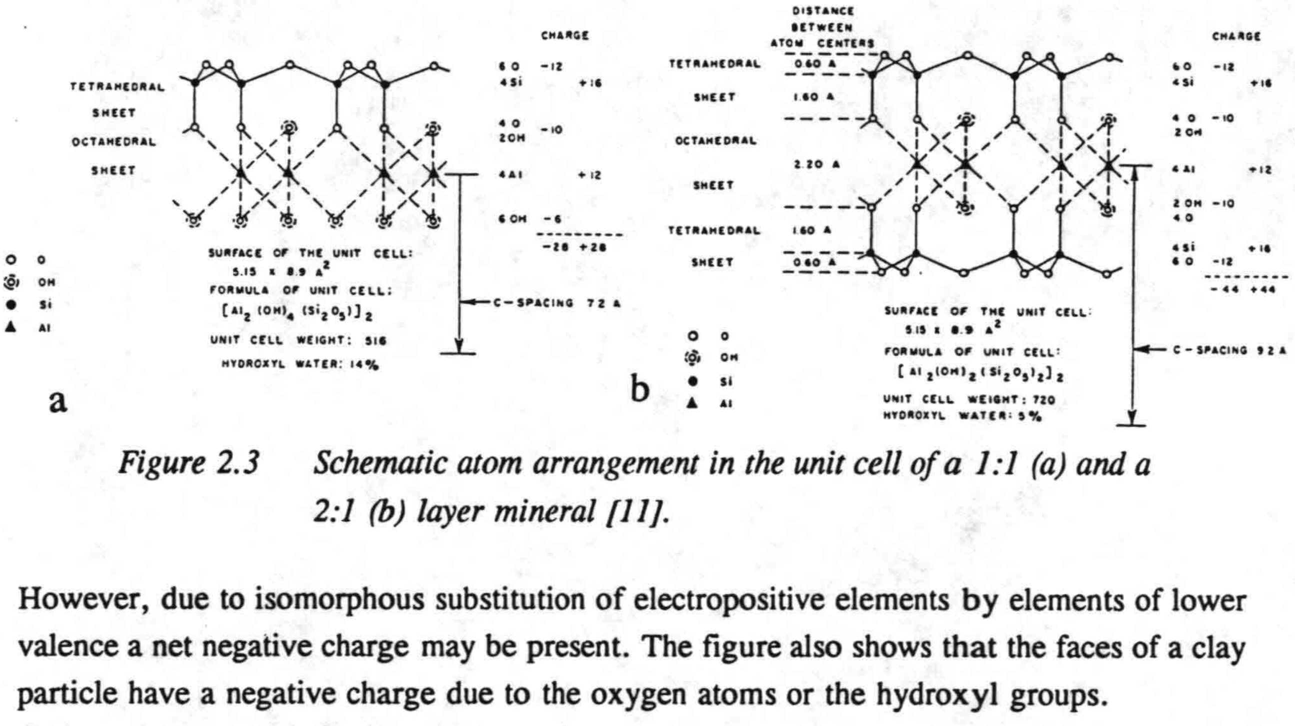

Figure 2.3 Schematic atom arrangement in the unit cell of a 1:1 (a) and a 2:1 (b) layer mineral [11].

However, due to isomorphous substitution of electropositive elements by elements of lower valence a net negative charge may be present. The figure also shows that the faces of a clay particle have a negative charge due to the oxygen atoms or the hydroxyl groups.

Cations are attracted, in the presence of water, to the negative charge on the faces of the particle, but these cations have also a tendency to diffuse away from the particle face since their concentration is lower in the bulk solution. The result of these opposing trends is the creation of a diffuse electrical double layer on the surface of a particle, also called Gouy layer. A schematic representation of it is shown in figure 2.4.

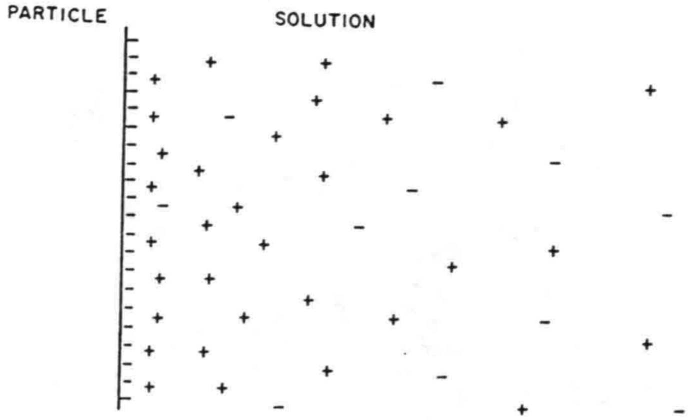

Figure 2.4 Diffuse electric double-layer according to Gouy [11].

The thickness of the Gouy double layer depends on variations in the cation valence ν, the dielectric constant of the medium D, the temperature T and the electrolyte concentration n_0. An approximate indication of the influence of these parameters on the thickness B of the double layer is given by [10]:

$$B \sim \sqrt{\frac{DkT}{8\pi n_0 e^2 \nu^2}} \tag{2.1}$$

where k is the Boltzmann constant ($1.3806 \cdot 10^{-23}$ JK^{-1}) and e is the unit electronic charge ($1.6022 \cdot 10^{-19}$ C) [15]. Furthermore, the thickness of the double layer is proportional to the natural logarithm of the surface charge density σ [10].

From this relationship it may be noted that the thickness increases with the square root of the dielectric constant and the temperature. The thickness decreases inversely proportional to the valence and the square root of the concentration.

The charge of the electric double layer is constant and is solely determined by the type and degree of isomorphous substitutions. Consequently, the presence of electrolytes in the suspension has no influence on the charge density on the particle face, but when the electrolyte concentration is increased the double layer is compressed towards the particle surface. Such a compression of the double-layer may also be achieved by the addition of water-miscible solvents, such as alcohols or acetones [4,5,6,13,14].

The faces of the particles are not the only surfaces of the plate-like clay particle. They also expose an edge surface, the structure of which is completely different from that of the faces. This difference is caused by the disruption of the tetrahedral silica sheets and the octahedral sheets at the edge of a particle. The atomic structure is very complex and it is not very easy

to make an estimation of the charge at the edge. However, from several observations [10,11,14] it may be concluded that the clay particle has a positive charge at the edge.
The compensating cations in the Gouy layer may be easily exchanged by other cations. The total amount of exchangeable cations may be determined analytically. This amount, usually expressed in milliequivalents per 100 g of dry clay, is called the Cation Exchange Capacity (CEC). (The number of ions in an equivalent equals Avogadro's number ($6.022 \cdot 10^{23}$ $mole^{-1}$) divided by the valence of the particular ion [15]).

3. Forces between clay particles

Essentially two forces dominate the interaction between clay particles in a suspension, namely the Van der Waals force and an electrostatic force generated by the electric double layer. Due to Brownian motion or turbulence, for instance, two particles may approach each other and the surrounding double layers will start to interfere. From electrostatic and diffusion theory (the Poisson-Boltzmann equation) it can be shown [8,10,11] that this interference

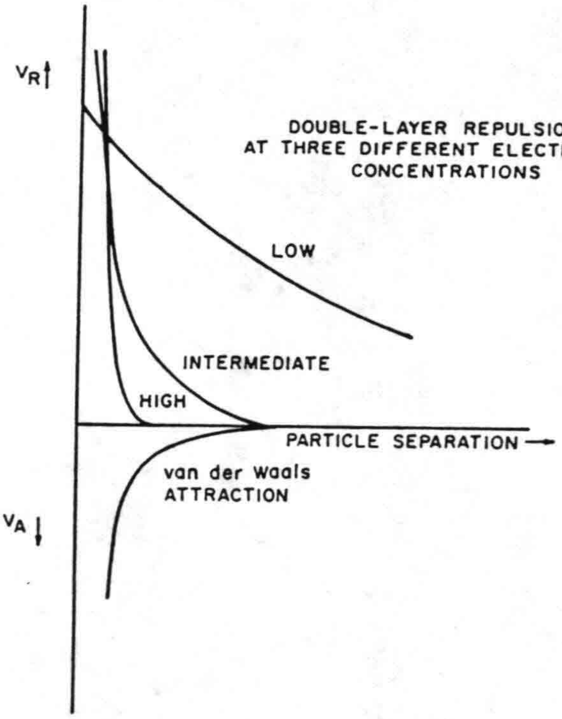

Figure 3.1 Repulsive and attractive energy as a function of particle separation at three electrolyte concentrations [11].

changes the distribution of the ions in both double layers. This change involves an increase in the free energy of the system, so there will be a repulsive force between the particles. The repulsive potential (V_R) as a function of the particle separation is shown in figure 3.1 for three different electrolyte concentrations. This figure shows that the range of repulsion is reduced due to the compression of the double layer at increasing electrolyte concentrations. In this figure is also drawn the attractive potential V_A of the Van der Waals force. For two atoms this force is inversely proportional to the seventh power of the distance and is almost independent of the electrolyte concentration of the medium. Due to the fact that the Van der Waals attraction between atom pairs is additive, the force is inversely proportional to the third power of the distance for two relatively large particles, such as clay particles [11].

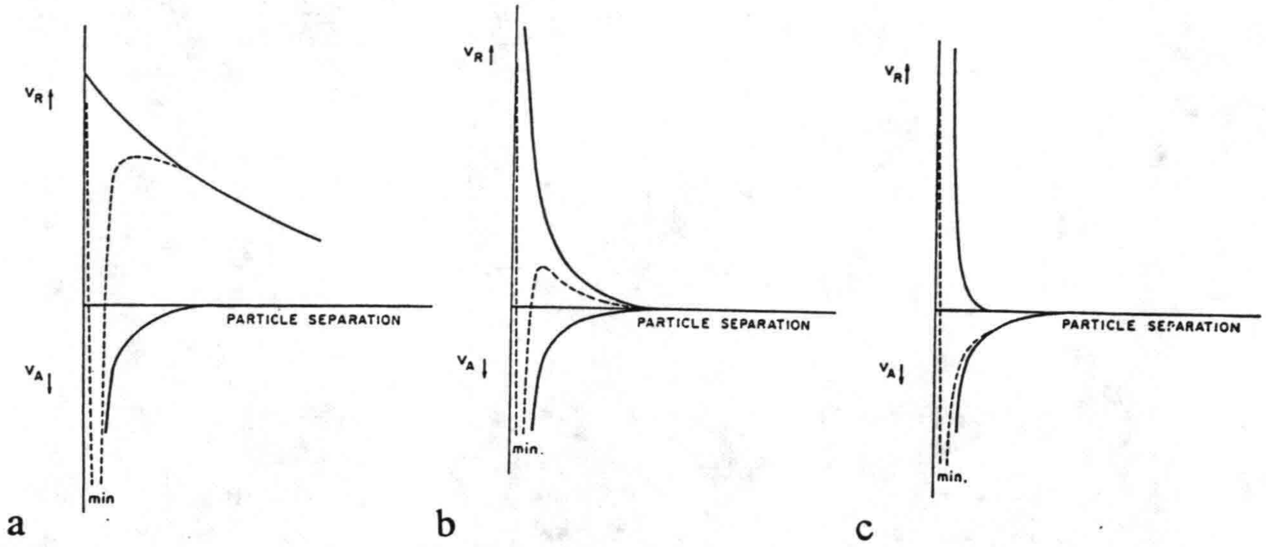

Figure 3.2 *Net interaction energy as a function of particle separation for low (a), intermediate (b) and high electrolyte concentrations (c) [11].*

The net interaction curve between two particles is found by adding the repulsive and the attractive energy. The (dotted) curves for the three different electrolyte concentrations are shown in figure 3.2. In the calculation of these curves an additional interaction force was taken into account. This interaction is a very strong repulsion at very short range, caused by the so-called Born repulsion and the specific adsorption forces between the crystal surface and the molecules of the liquid medium.

The curves in figure 3.2 show that there is almost no repulsion at high electrolyte concentrations, which results in a maximal particle agglomeration rate. This process is also called rapid coagulation. For lower electrolyte concentrations (low and medium) the particles have to overcome a repulsive energy barrier to coagulate, yielding a slower coagulation rate. For reasons of simplicity the previous description of the double layer interaction has been based on the Gouy model of the electric double layer. However, the assumptions made in this model are not quite realistic, because the ions are treated as point charges, for instance. Stern was the first who created a more realistic model (1924). He argued that the distance of closest approach of a counter-ion to the charged surface is limited by the size of the ion. The accumulated ions of an opposite sign are called counter-ions. Consequently, the counter-ion charge is more or less separated from the surface charge by a layer of thickness δ in which there is no charge. In this so-called Stern layer the electric potential drops linearly with distance, from a value ϕ_0 at the surface to a value ϕ_δ. The latter value is also called the Stern potential. A further increase in the distance results in a decreasing electric potential like in a Gouy layer. A representation of this model is shown in figure 3.3.

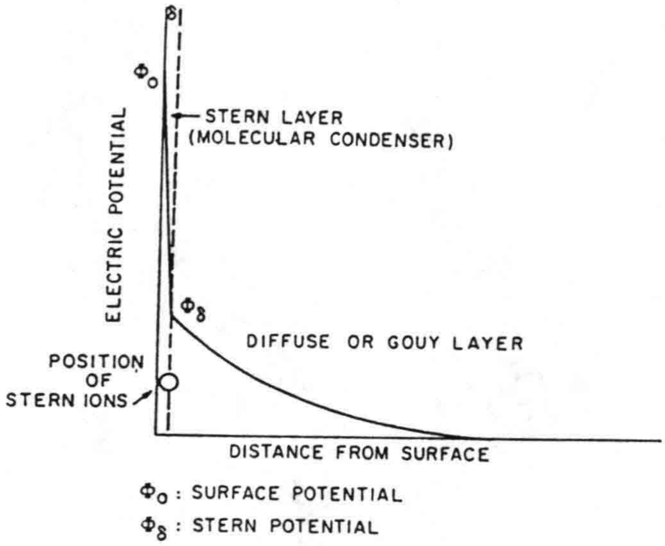

Figure 3.3 *Stern's model of the potential distribution in the electric double layer [11].*

The result of the addition of electrolyte in the Stern model is not only a compression of the diffuse (Gouy) part of the double layer, but also a shift of the counter-ions from the diffuse layer to the Stern layer and hence in a decrease of the Stern potential.

For further improvements of the theory see [10,11], for instance.

4. Flocculation

Continual coagulation of clay particles results in the formation of flocs. Three different modes of coagulations may occur in a suspension of platelike clay particles, namely face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE). These three modes will not necessarily occur simultaneously or to the same extent when a clay suspension is flocculating. This is a consequence of, among other things, the different Van der Waals interaction energy and the electrical interaction energy of the double layers of the three modes.

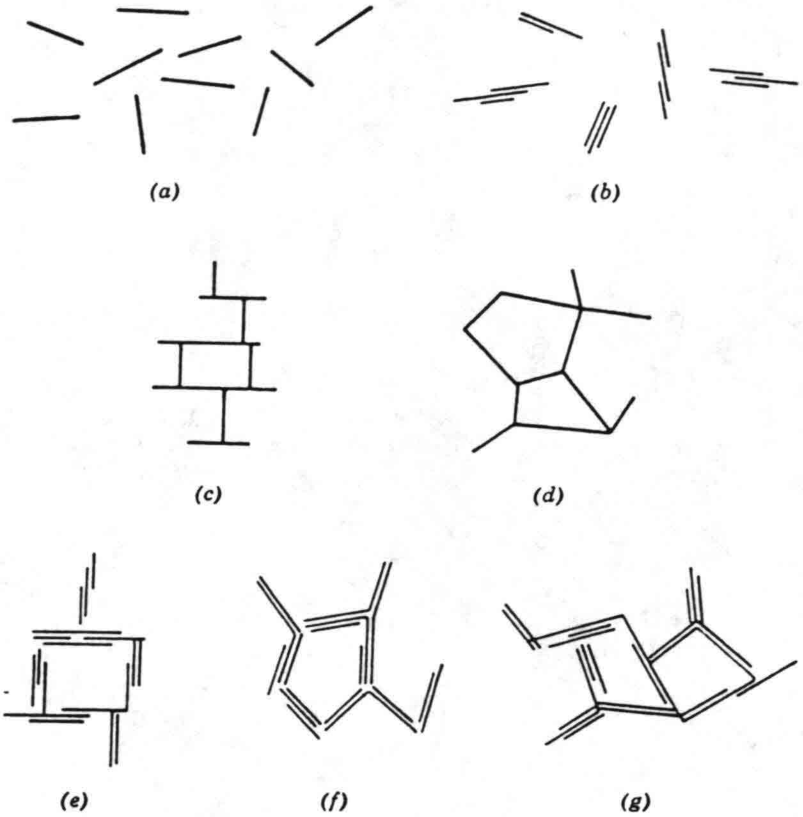

Figure 4.1 *Particle association modes in clay suspensions. (a) dispersed and deflocculated, (b) aggregated but deflocculated (FF association), (c) EF flocculated but dispersed, (d) EE flocculated but dispersed, (e) EF flocculated and aggregated, (f) EE flocculated and aggregated, (g) EF and EE flocculated and aggregated [11].*

The various modes of particle association in clay suspensions are represented schematically in figure 4.1. This figure shows that only the EE and the EF types of association lead to agglomerates which can be called flocs. The thicker FF type agglomerates are called aggregates. The dissociation of EF and EE linked particles is described as deflocculation, whereas the dissociation of FF associated aggregates is described as dispersion.

The face-to-face association results in thicker and possibly large flakes, whereas EF and EE associations result in three-dimensional, voluminous card-house structures. It is obvious that the properties of a flocculated suspension are dependent on the mode in which the particles are flocculated. The principal relations between flow behaviour and particle interaction may be summarized briefly as follows [1,11,14].

For dilute clay suspensions the viscosity increases when conglomerates are formed by EE and EF association. The viscosity decreases when the particles become thicker by FF association. In concentrated clay suspensions continuous, linked, card-house structures are formed by EE and EF associations, which extend throughout the total available volume. Such suspensions appear to behave as 'Bingham systems'. Such a system is characterized by a Bingham yield stress, which is a measure for the number and strength of the links in the card-house structure. If FF association occurs simultaneously the Bingham yield stress will decrease, because the number of units building the card-house structure is reduced and hence the number of links decreases.

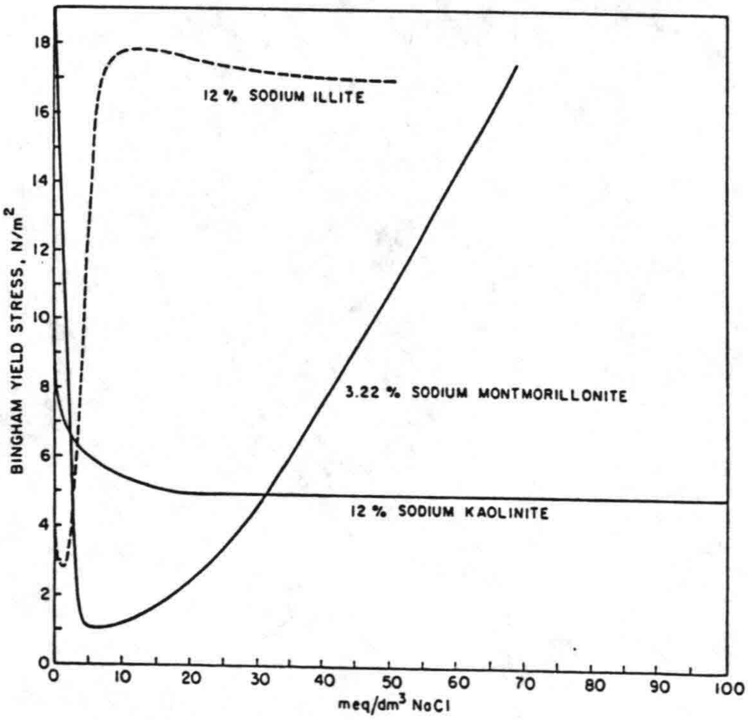

Figure 4.2 *Bingham yield stress of clay suspensions as a function of the amount of added NaCl [11].*

In figure 4.2 an example is shown of systems in which the flow properties change when increasing amounts of electrolyte are added. The Bingham yield stress is plotted along the vertical axis as a function of the amount of NaCl added, which is plotted along the horizontal axis. The suspended sediment concentration of the clay suspensions is expressed in percentage of the total weight.

When no electrolyte is added, both double layers on the clay particles are well developed so that particle association by Van der Waals attraction is prevented. However, EF association takes place owing to the opposite charges of the edge and the face double layers. This feature causes a relatively high yield stress. In a dilute system this feature will cause a relatively high viscosity.

In the presence of a few milliequivalents of electrolyte, both double layers are compressed. Consequently, both the EF attraction and the EE and FF repulsion will diminish. The particles will become disengaged and hence the yield stress is dramatically reduced. In dilute suspensions, the conglomerates are dispersed, and the viscosity will decrease.

Further increasing the amount of electrolyte causes a further compression of the double layers. The Van der Waals attraction between edges and faces enhances what remained of the opposite-charge attraction and the subtle balance between EF attraction and FF repulsion seems to become favourable for the formation of the card-house structure. Furthermore the possible EE association by Van der Waals attraction may contribute to the resulting increases in yield stress and viscosity of dilute suspensions.

At high electrolyte concentrations, the yield stress tends to decrease a little. This observation, which is not shown in figure 4.2, may be explained by the simultaneous occurrence of FF association by which the number of particles is reduced.

The stated features of the sodium illite system discussed above are often less pronounced, or even absent, for other clays. This may be caused by the fact that one type of association is dominating in a wide salt-concentration region. A sodium kaolinite system, for example does not show the spectacular increase in yield stress at moderate salt concentrations, see figure 4.2. In this system FF association seem to dominate as soon as the EF links have been weakened by the addition of a small amount of salt. In other clays, for instance calcium montmorillonite, the initial sharp decrease in yield stress does not occur.

Summarizing, it seems that different clays react differently on the addition of electrolyte because of the differences in their initial double-layer structures.

An other example of the influence of a flocculating agent on a suspension of clay is shown in figure 4.3. The electrolyte is the cationic organic polymer PEE (ethanolamine-epichlorhydrine polycondensate) and it is added to a suspension of montmorillonite in water. The polycations are strongly adsorbed on and almost entirely attached to the negative surface of the clay particle. The flocculation occurs as a consequence of the compression of the double layer. This type of flocculation requires very distinct conditions of salt and clay concentrations [7]. Furthermore, the polycations can penetrate between the layers, but complete coverage of the internal surfaces is rarely achieved.

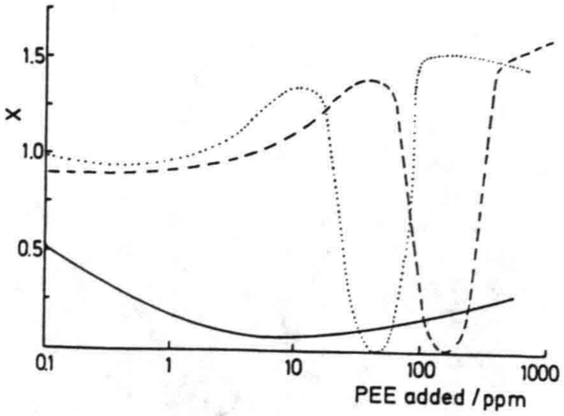

Figure 4.3 *Flocculation of montmorillonite by the cationic polymer PEE; X = amount of montmorillonite + PEE (ads.) in solution/total amount of montmorillonite; dotted line: 100 mg/l, deionized water; dashed line: 300 mg/l, deionized water; line: 100 mg/l, natural water [7].*

The influence of an other organic polymer on the properties of clay is shown in figure 4.4. In this figure the fabric of montmorillonite and kaolinite is shown in the presence of two polysaccharides, namely Dextran and Slceroglucan. Dextran is a specific bacterial secretion and Slceroglucan is a fungal slime, both are neutral glucose polymers having molecular weights of about $2 \cdot 10^6$ and $1.5 \cdot 10^6$, respectively. However, the structures of the polymers

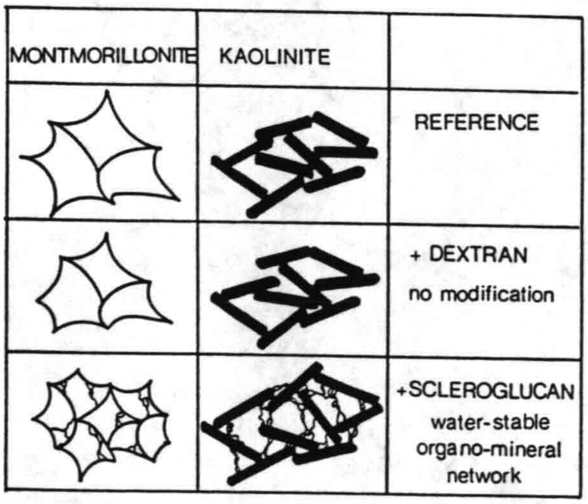

Figure 4.4 *Schematic representation of the fabric of Ca-kaolinite and Ca-montmorillonite in the presence of polysacchararides [3].*

is quite differently; Dextran has a random coil conformation and Scleroglucan occurs in a solution as a aggregated triple helix. The polysaccharides have a different effect on the fabric, although the molecular weights are almost the same. Only in the presence of Scleroglucan polysaccharide bridges between the clay particles were found, resulting in a more stable aggregate. For more information the reader is referred to [3].

5. Deflocculation of clay suspensions

A clay suspension is rather stiff when it is in a flocculated condition, which makes it rather difficult to handle, for instance in the drilling-mud technology. This stiff suspension could be turned into a more fluid system by breaking the particle links. This can be done by reversing the positive edge charge and creating a well-developed negative edge double layer. The positive-edge-to-negative-face attraction would then be eliminated and a strong EE as well as EF repulsion would be created, resulting in a breakdown of the flocs.

A variety of chemicals are known which are able to liquefy a clay suspension, for instance inorganic salts, alkalies and organic compounds. These chemicals are usually called peptizers. Only a small amount of these peptizers added is necessary to decrease the yield stress of a suspension. This effect, the so-called peptization, is comparable with that of a small addition of salt, for instance NaCl. Further addition of peptizer has little effect on the yield stress. It remains low, as opposed to the rise observed with the further addition of salt. The yield stress begins to increase only at very high concentrations of peptizer.

If salt or another electrolyte is added to a system after a small amount of peptizer has been added, the yield stress remains low, unless a rather large amount of salt is added.

In dilute clay suspensions the effect of the peptizer on the flocculation and deflocculation correlates with the observed decrease and increase in yield stress in more concentrated clay suspensions.

The results of deflocculation-flocculation experiments with peptizers and salts can be presented in a flocculation diagram, in which the salt-flocculation value of the clay is plotted versus the amount of peptizer present in a suspension. The salt-flocculation value is the minimum concentration of salt which causes the flocculation of a certain clay mineral in a given time. The usually obtained result of such an experiment is shown in figure 5.1, curve 1. The flocculation value of a treated suspension increases quite rapidly with increasing peptizer concentration, until a maximum is obtained. Further addition of peptizer results in a decrease in salt flocculation value, due to the flocculation action of the peptizing salt. Finally, at relatively high concentrations of the peptizer, the clay flocculates with the peptizer alone. The flocculation value of the peptizing salt is however much higher than that of salt. This behaviour of clay in the presence of two electrolytes is called antagonism.

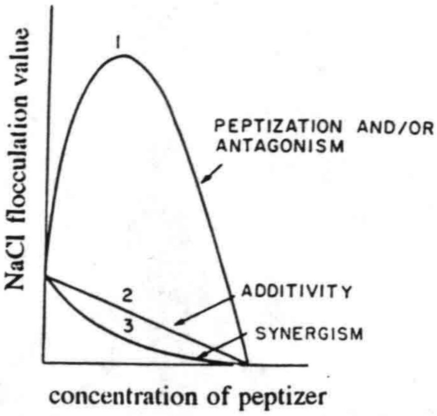

Figure 5.1 *Effects of a mixture of two electrolytes on the stability of a clay particle [11].*

Two more curves are drawn in figure 5.1 which represent other possible effects. If the electrolytes are of the same type, such as for instance NaCl and KCl, and if there are no special interactions between the suspended particles, the flocculation values are usually additive, see curve 2 in figure 5.1. If clay particles are made more susceptible for flocculation by an electrolyte in the presence of an other electrolyte, one can speak of synergism. Curve 3 is an example of this type of flocculation.

6. The mechanism of peptization

From observations it may be concluded that the basic mechanism of chemical clay peptization is the reversal of the positive edge charge by anion adsorption into a negative one. In this way, both EF and EE associations of the clay plates would be eliminated causing deflocculation.

Knowing this mechanism, it is clear why such small amounts of peptizing chemicals have such a spectacular effect on the rheological behaviour of a flocculated clay suspension: the small edge surfaces need very little amounts of peptizer to build a negative double layer. The anions will be attracted by the positive edge surface. However, the electrostatic attraction of the anions alone would lead to a neutralization of the edge. Considering the types of peptizing anions that are known, it appears that they have in common a specific reactivity with aluminium, with which they either form complex anions or insoluble salts.

When complex anions are formed, as is the case with polymetaphosphates, the creation of a negative double layer is easy to understand. In figure 6.1 a schematic representation is shown of a polymetaphosphate anion attached, with a fraction of its ionic groups, to a number of charge sites at the edge of a clay particle. The remaining negative groups of the anion build up the negative charge.

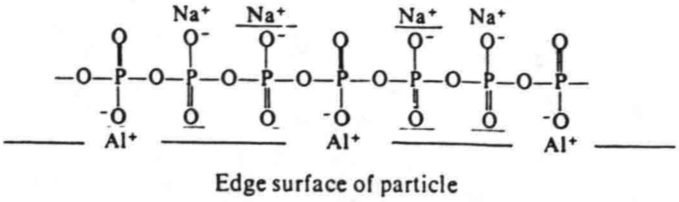

Figure 6.1 *Schematic representation of an adsorbed polymetaphosphate ion on a clay particle [11].*

If an insoluble, neutral aluminium salt is formed, it seems likely that the additional anions will be preferentially adsorbed on the formed aluminium salt. These anions will act as potential-determining ions for the modified edge surface.

As said before, alkalies may have some peptizing effect on clay suspensions. With certain clay suspensions such an effect has been observed, for instance with kaolinite particles. However, in general the peptizing effect is much less pronounced than that with peptizing salts.

A change in pH strongly causes the tendency of a hydroxyl (OH), exposed on the surfaces and edges, to dissociate ($SiOH \rightarrow SiO^- + H^+$). The higher the pH, the greater the tendency of the H^+ to go in solution and the greater the effective negative charge of the particle becomes. As a consequence the positive charge at the edge may disappear and a net negative charge may be created, causing deflocculation. This effect plays an important role with kaolinite. It is lesser important with illite and relatively unimportant with montmorillonite. For kaolinite the pH may be the most important factor controlling the fabric of flocs formed from suspension.

Knowing the mechanism of peptization it is clear that different clays respond quite differently to the same peptization salt. Clays often differ in the type of substituting ions in the octahedral sheet. Consequently, in different clays different cations will be exposed at the broken edges resulting in an other response on the peptizing salt.

Although the above mentioned peptizing mechanism is the principal one, there are still two factors which contribute to the increase in salt flocculation value of treated clay suspensions, namely cation activity reduction and conversion of a clay into another form by ion exchange. These factors will not be described here, because their effect is relatively small [10,11].

An other, fluid-related, factor is the Sodium Adsorption Ratio (SAR) which is defined by the following expression:

$$\mathrm{SAR} = \frac{\mathrm{Na}^+}{\left(\tfrac{1}{2}\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)\right)^{1/2}} \tag{6.1}$$

where the cation concentrations are in milliequivalents per litre. The SAR represents the ratio of Na^+ ions with respect to the Ca^{2+} and Mg^{2+} ions in the pore water and can be determined by a chemical analysis. The SAR is in fact a term in a practical form of the so-called Gapon equation, namely

$$\left[\frac{\mathrm{Na}^+}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}\right]_s = c\,[\mathrm{SAR}]_e \tag{6.2}$$

where the subscript *s* refers to the exchange complex of the clay, the subscript *e* refers to the equilibrium solution and c is a selectivity constant. The value of this constant is 0.017 for a wide range of soils. If the composition of the pore fluid is known (SAR), the relative amounts of monovalent and divalent ions in the adsorbed cation complex can be estimated. The influence of the SAR on the particle interaction can be illustrated by the following example. Suppose a suspension of clay particles in a waterbased electrolyte. Only Na^+, Ca^{2+} and Mg^{2+} ions are present in the electrolyte. The total number of ions is constant, only the ratio of concentrations of the different ions is variable. If the SAR value is low, the diffuse double layer will be compressed due to relatively high concentration of the divalent Ca and Mg ions. Consequently the inter-particle attraction will increase. If the SAR value is high, a relatively high concentration of Na ions will extend the diffuse double layer, causing an increase in the inter-particle repulsion [2,10].

7. Properties of different types of clay minerals

As mentioned before, several clay minerals exist, which all have different properties depending on the structure of the mineral. The properties of the most common minerals will be discussed hereafter [10,11,12].

7.1 Smectites (2:1 layer clays)

The smectites are known as the expanding three-layer clays and have a structure that consists of an octahedral sheet sandwiched between two silica sheets, see figure 7.1.1. A stack of such layers is forming a smectite particle. Minerals of the smectite group are montmorillonite, bentonite and hectorite, for instance. The bonding between the successive layers is through Van der Waals forces and through cations that may be present to balance charge deficiencies in the structure. These bonds are relatively weak and may be easily

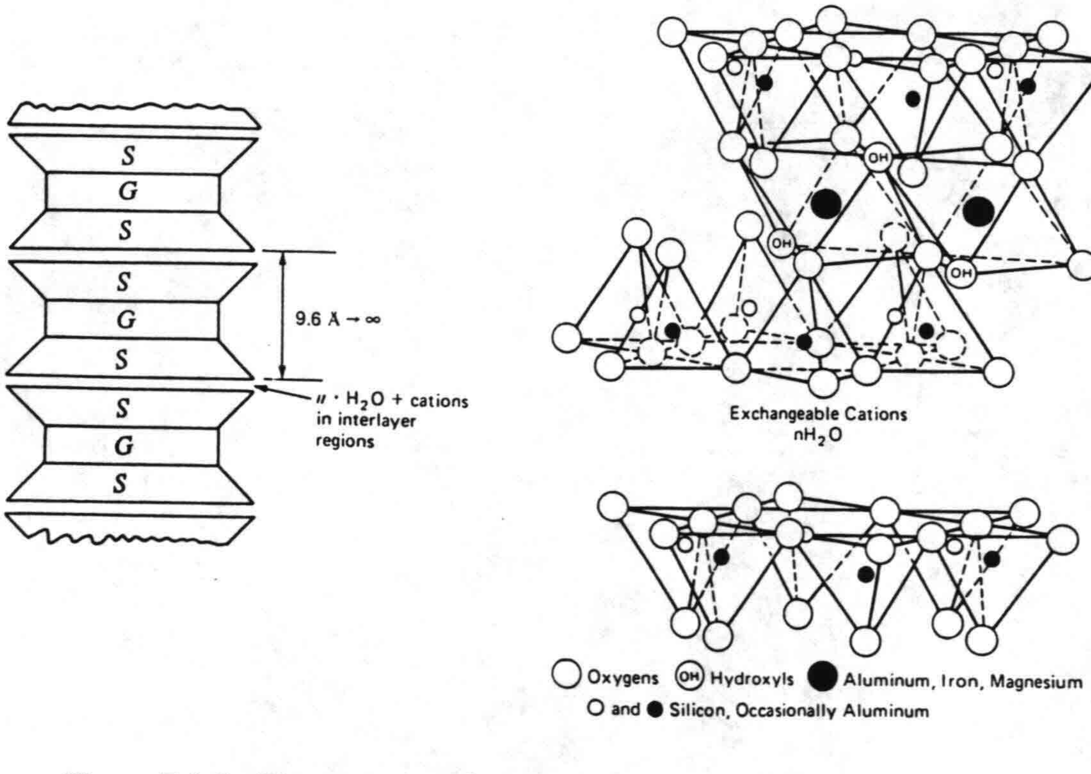

Figure 7.1.1 The structure of montmorillonite [10].
G : Gibbsite sheet
S : Silica sheet

broken by cleavage or adsorption of water. When smectite clays are contacted with water the water molecules penetrate between the layers. This feature of smectite clays is usually called interlayer - or intra-crystalline swelling and can lead to a doubling of the volume of originally dry clay when four layers of water molecules are adsorbed. However, an even larger swelling or expansion is observed for many smectite clays. This is caused by another mechanism, namely osmotic swelling [10,11], which will not be described here.

Smectites are also characterized by the extensive substitution of aluminium an silicon ions within the lattice by other ions, which results in a charge deficiency. Aluminium in the octahedral sheet may be replaced by magnesium, iron, zinc, nickel or other cations, and in the silicon sheet up to 15 % of the silicon may be replaced by aluminium. In montmorillonite for instance one Mg^{2+} is substituted for every sixth Al^{3+} in the octahedral sheet. Due to the large amount of unbalanced substitutions the smectite clays have rather high cation exchange capacities, namely in the order of 80 to 150 meq/100g.

The smectite particles have the tendency to be very small, because the bonds between the layers are very weak. Montmorillonite usually occurs as filmlike flakes with a thickness ranging from 10 Å to about 1/100 of the width. The length of the long axis of the flake is usually less than 1 or 2 μm.

The specific surface area of the smectites is very large. A distinction can be made between a primary surface and a secondary surface. The primary specific surface is the particle surface excluding the surface of the interlayer zones. Its area is generally about 50 - 120 m^2/g. The secondary surface area, which may be exposed by expanding the lattices, may range from 700 to 840 m^2/g.

7.2 Illites (nonexpanding 2:1 layer clays)

Illite clays form a different class of the three-layer clays. These clays are distinguished from the smectite clays primarily by the absence of interlayer swelling with water. About one quarter of the silicon in the silicon sheet is substituted by aluminium. Potassium ions between the layers compensate the net negative layer charge generated by the substitution of aluminium. These potassium ions are fixed and due to a specific electrostatic linking effect of these ions the layers do not part upon the addition of water. The potassium ions establish an electrostatic linking of the separate layers, see figure 7.2.1. Only potassium ions on the external surface may be exchanged.

The minerals muscovite and phlogopite, for instance, are minerals of the illite group.

The cation exchange capacity of illite is less than that of smectites because of the

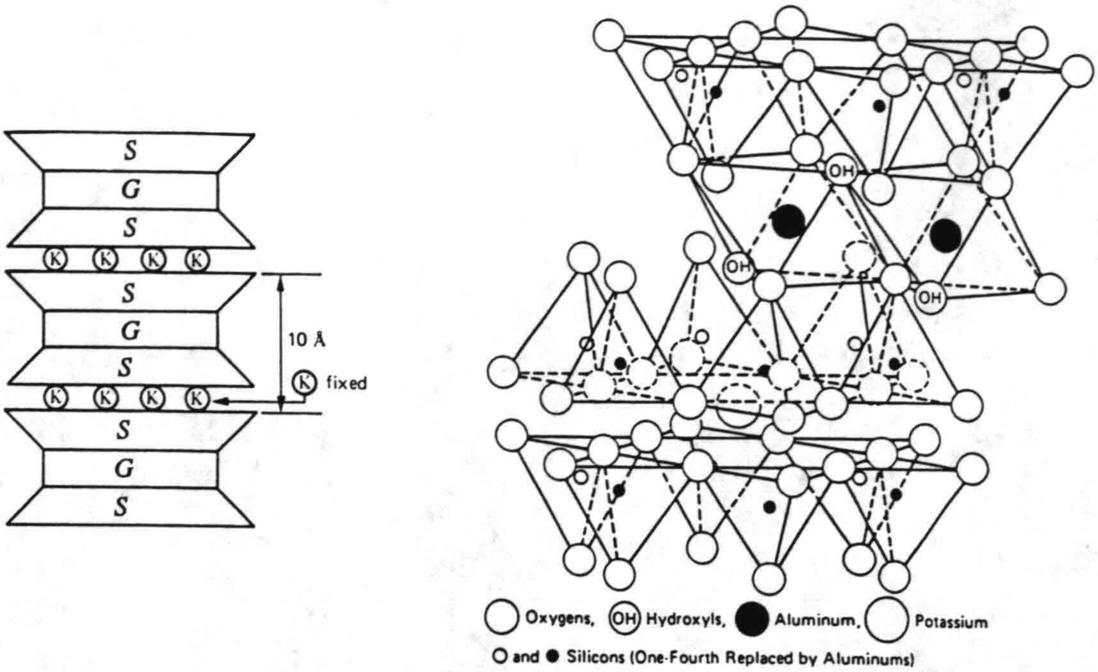

Figure 7.2.1 Structure of muscovite [10].
G : Gibbsite sheet
S : Silica sheet

nonexchangeable potassium ions and varies between 10 and 40 meq/100g.
The particles are usually flaky and very small. If they are well crystallized, they have a hexagonal outline and the long axis dimension ranges from 0.1 μm to several micrometers. The thickness of the flake may as small as 30 Å. The specific surface area is about 65 - 100 m^2/g.

7.3 Kaolinites (1:1 layer clays)

The clay minerals of the kaolinite group have an almost perfect 1:1 layer structure. The main difference between the various species is a difference in layer stacking geometry. Members of this group are for instance kaolinite, dictite, nacrite and halloysite. The kaolinite clays are nonexpandable in water. A schematic representation of the structure of kaolinite is given in figure 7.3.1.
The cohesive energy is primarily electrostatic. However, the Van der Waals attraction and

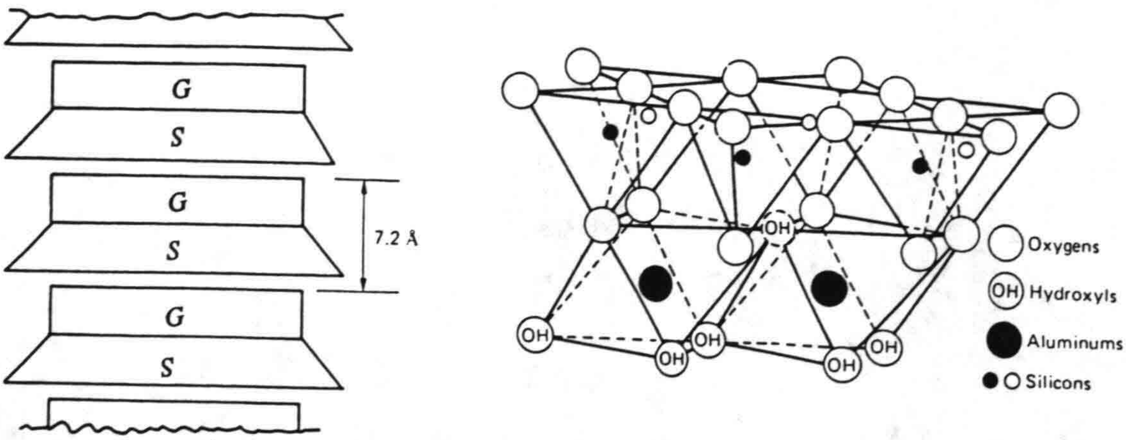

Figure 7.3.1 The structure of kaolinite [10].
G : Gibbsite sheet
S : Silica sheet

a certain degree of hydrogen bonding, between the hydroxyl groups of one layer and the oxygen atoms of the adjoining layer, amplify the cohesive energy.

The cation exchange capacity of the kaolinite minerals is quite low, namely 3 - 15 meq/g, which corresponds with, a replacement of one Si^{4+} for one Al^{3+} in every 400 for instance. Well crystallized particles of kaolinite are shaped like a six-sided plate. The length of such a particle varies from 0.1 to 4 μm and their thickness varies from 0.05 to 2 μm. However, stacks of kaolinite layers have been observed with a thickness of up to 4000 μm. Less crystallized kaolinite particles usually have a less distinct hexagonal shape and they are smaller than the well crystallized particles.

The specific surface area of dry kaolinite is of the order of 10 to 20 m^2/g.

For more flocculation characteristics of kaolinite the reader is referred to [14].

8. Conclusions

In this report a basic overview is given of the properties of clay. However, it is impossible to describe all features of clay, because the influence of (in)organic substances on the interaction of clay particles is very complex.

The properties of mud, which consists of clay and other (in)organic substances is even more complex, which makes it very difficult to predict its behaviour. Peptizing salts, for instance, may destruct the flocs in a suspension or decrease the strength of a bed, resulting in highly mobile suspension or in an easy erodible bed, respectively. Only small quantities of peptizers are necessary to cause radical changes in the behaviour of mud. On the other hand, small amounts of flocculating salts may cause a rapid coagulation of particles, resulting in a large sedimentation rate.

Consequently, from an hydraulic engineering point of view it is essential to have a general understanding of the properties to be able to predict the transport of mud. However, a lot of research has still to be done until our knowledge of mud is large enough to predict its behaviour.

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