Física do Solo
CCR/UFSM

Argilominerais

Eletroquímica de colóides (Dupla camada difusa)

J. Miguel Reichert, PhD

(Oregon State Univ.; prof. R. Horn-Kiel Univ.;
prof. M.K. Shukla-Arizona St. Univ.; prof. N. Sivakugan, e outros)

Clay Minerals

Clay minerals are secondary minerals

- Clays have been chemically altered, or have undergone chemical weathering
- Clay minerals are highly reactive materials with electrically charged surfaces.
- All clay minerals are made up of individual clay particles
- Clay properties result from the arrangement of these individual clay particles

Soil Colloid

- In Greek colloid means “glue-like.”
- Organic or inorganic matter with very small particle size and a corresponding large surface area per unit mass.
- Less than 0.001mm in size

A Comparison

Mineral	Specific surface (m^2/g)	C.E.C (meq/100g)
Kaolinite	10-20	3-10
Illite	80-100	20-30
Montmorillonite	800	80-120
Chlorite	80	20-30

Soil Colloids

4 TYPES

Crystalline Silicates

1:1, 2:1 (expanding and non-expanding), 2:1:1

Non-Crystalline Silicates

Allophane and Immogolite (products of volcanic ash)

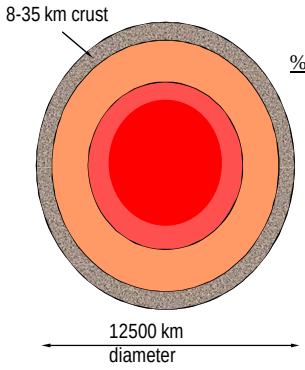
Fe and Al Oxides / Hydroxides / Oxyhydroxides

Geothite, Gibbsite, Hematite, Ferryhydrite, Maghemite

Organic Matter (humus)

High and Low Molecular Weight Acids (Fulvic, Fluvic, Hemic)

Elements of Earth

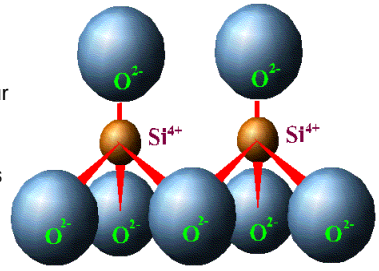


% by weight in **crust**

O	= 49.2	82.4%
Si	= 25.7	
Al	= 7.5	
Fe	= 4.7	
Ca	= 3.4	
Na	= 2.6	
K	= 2.4	
Mg	= 1.9	
other	= 2.6	

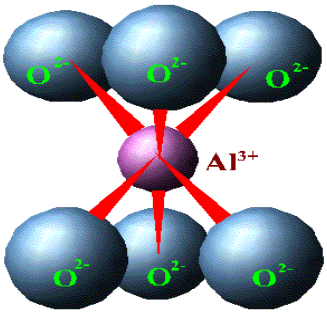
The Simplest Structure

- **Tetrahedron**
  - One silicon ion surrounded by four oxygen atoms.
- Tetrahedral sheets
  - Tetrahedral sheets are joined by shared oxygen atoms

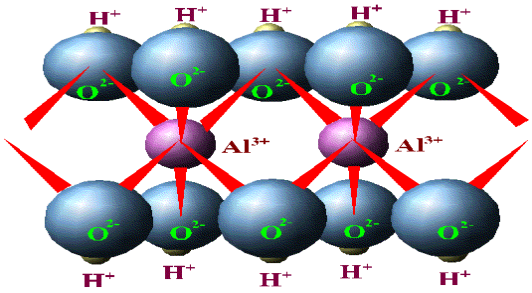


The Eight-sided Octahedron

- **Octahedron**
  - Six oxygen with a central Al^{3+} atom
- Octahedral sheet
  - Octahedral sheets are linked together by shared oxygen

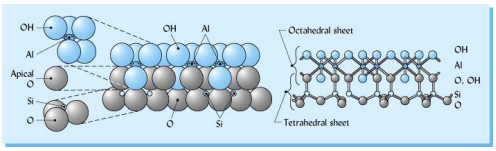


Octahedral Sheet



Clay Mineral Structure

- Clay particles are composed of tetrahedral and octahedral layers stacked on top of each other.



Water and Clays

- When clays become wet, they exhibit different properties which are related to their structure
- These properties include: (1) plasticity, (2) stickiness, (3) cohesion, (4) shrinkage and (5) swelling
- Of major importance is shrink/swell capacity

Result of Shrink/Swell in clay soils

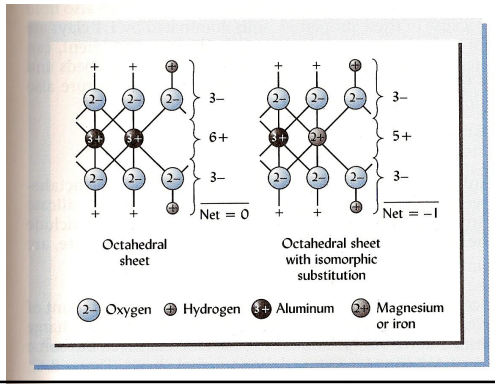
Isomorphous Substitution

- **Isomorphous Substitution**

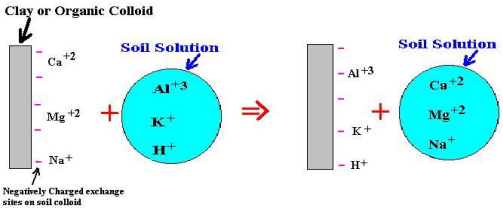
  Replacement of one atom by another atom of similar size in the crystal lattice without disrupting or changing the crystal structure of the mineral.

- **In tetrahedral sheets-**
  - Al^{3+} can be substituted for Si^{4+}
- **In octahedral sheets-**
  - Mg^{2+} can be substituted for Al^{3+}
- **Importance-**
  - Causes unbalanced internal negative charge in the layers.
  - Unbalanced negative charges are compensated by the absorption of ions on the edges of clay particles

Isomorphic Substitution



Cation Exchange Illustrated



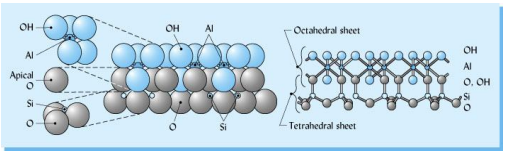
- Cation exchange- the interchange between a cation in solution and another cation on a soil surface
- Cation exchange capacity (CEC)- the total sum of exchangeable cations that a soil can adsorb.

Types of clays (1:1 and 2:1 clays)

- The arrangement of tetrahedral and octahedral sheets within the layers are used to classify clay type.
- **1:1 clays** exhibit one tetrahedral layer and one octahedral layer
- **2:1 clays** exhibit one octahedral layer between two tetrahedral layers

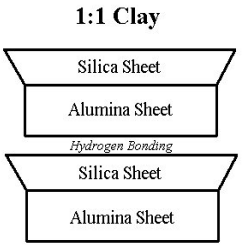
1:1 clays

- Kaolinite is a typical 1:1 clay
- One silicon tetrahedral sheet and one aluminum octahedral sheet
- Bonding:
  - A plane of oxygen atoms are exposed on the surface of the tetrahedral sheet and a plane of hydroxyls on the octahedral sheet.



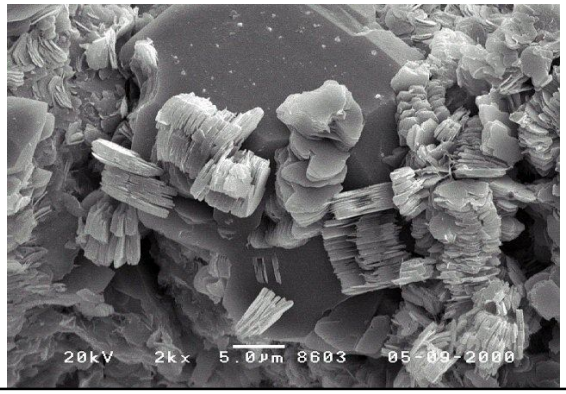
Kaolinite (1:1 clay)

- When one layer of kaolinite lies above a separate layer of kaolinite, the layers of alternating tetrahedral and octahedral sheets are literally stacked
- The hydroxyls of the octahedral sheet (bottom of the alumina sheet) are adjacent to the oxygen's of the tetrahedral sheet (top of the silica sheet), which permits adjacent layers to be bound by **hydrogen bonding.**

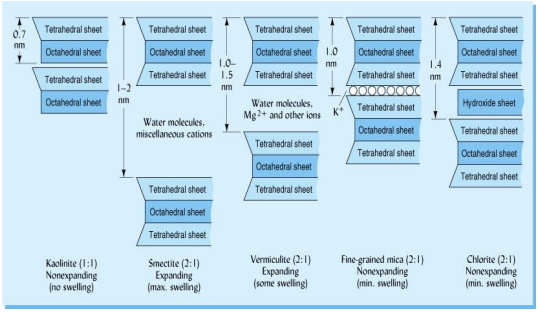


Kaolinite (SEM)

Kaolinite sheets on a Quartz Crystal

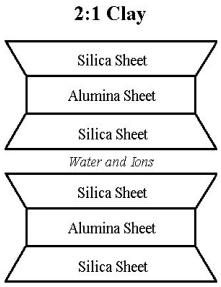


Summary of Clay Structures



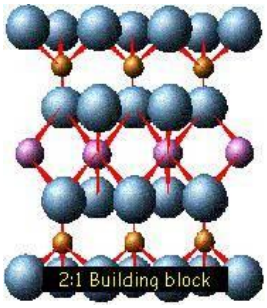
2:1 clays

- 2:1 clay minerals have one octahedral sheet between two tetrahedral sheets
- These clays include:
- (1) Smectite (Montmorilinite)
- (2) Vermiculite
- (3) Illite
- (4) Chlorite (2:1:1)



Mineralogical Organization of 2:1 Clays

- Tetrahedral sheet
- Octahedral sheet
- Tetrahedral sheet



Smectite Clays (2:1) Expanding

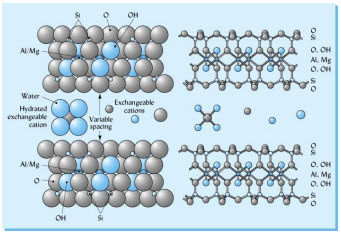
- The **smectite group** has a high amount of negative charge resulting from **isomorphic substitution**
- This process affects the overall charge of the mineral, making the layer more negative

Smectite Clays

- Within a smectite clay
  - Mg^{2+} ions can be substituted in the Al^{3+} positions of the octahedral sheet
  - Al^{3+} for Si^{4+} in the tetrahedral sheets
- The most common clay in the smectite group is Montmorilinite

The Smectite Group (2:1) Expanding

- There is little attraction between oxygen atoms between smectite layers,
- As a result, exchangeable cations and associated water molecules are strongly attracted to the spaces between the layers, which results in high shrink swell capacity **(1-2 nm)**

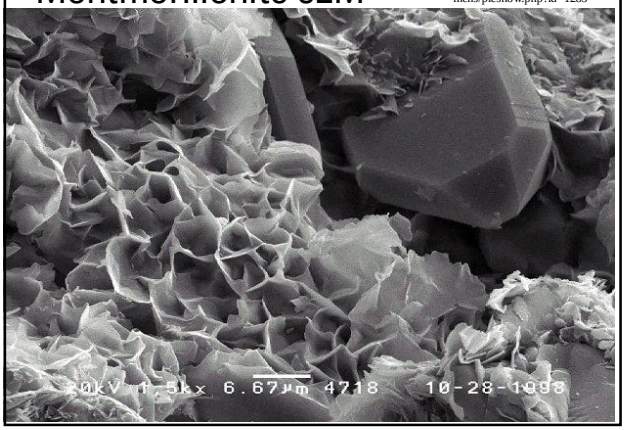


Note: The expansion within the interlayer water contributes to high plasticity, stickiness and cohesion

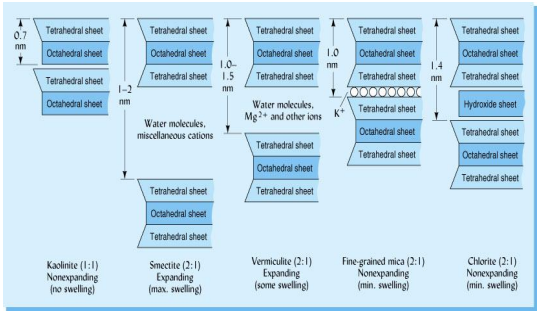
Smectite are very sticky when wet and very hard when dry

Montmorillonite SEM

http://webmineral.com/specimens/picshow.php?id=1285



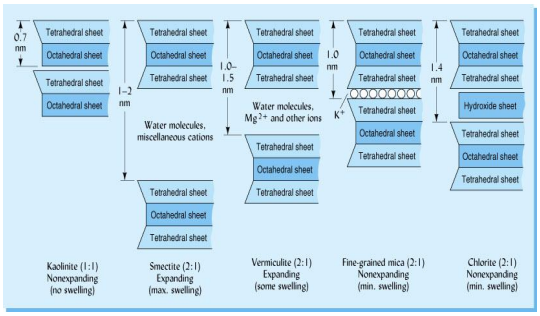
Summary of Clay Structures



Vermiculite (2:1) Expanding

- Al^{3+} usually dominates the octahedral sheet but some magnesium-dominated vermiculites exist.
- The tetrahedral sheets of most vermiculites have a lot of aluminum substitution for silicon, which creates a large negative charge.
- Highest CEC of all clays.
- Interlayer constituents act as bridges, which physically hold the layers together and reduces swell capacity.
- **SOME SWELL CAPACITY (1.0-1.5 nm).**

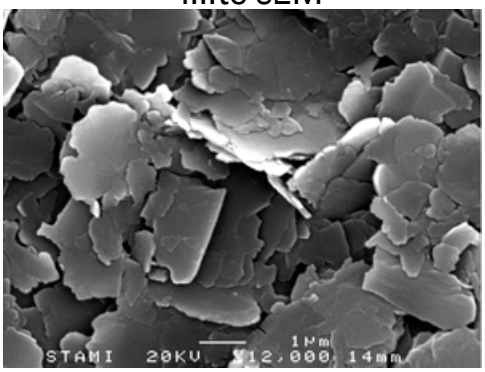
Summary of Clay Structures



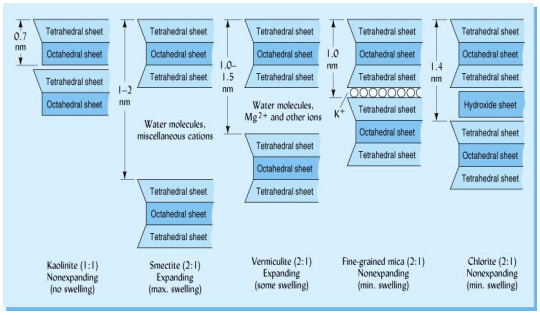
Fine Grained Mica's--Illite (2:1)

- Biotite and muscovite
  - Are unweathered micas found in sand and silt fractions.
- Illite
  - The clay formed from weathered biotite and muscovite.
- Al^{3+} for Si^{4+} substitution in the tetrahedral sheet
  - Creates a high net negative charge in the tetrahedral sheet.
  - Higher than in vermiculites.
- This high charge attracts cations
  - **Potassium Fixation-** Potassium (K+) becomes fixed between the layers

Illite SEM



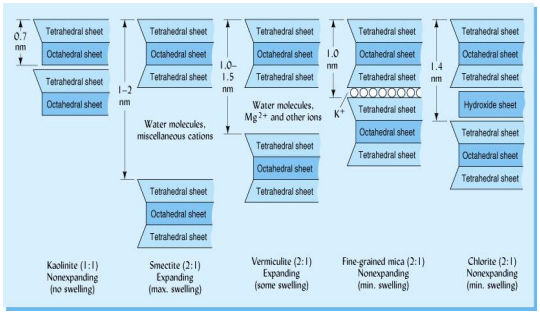
Summary of Clay Structures



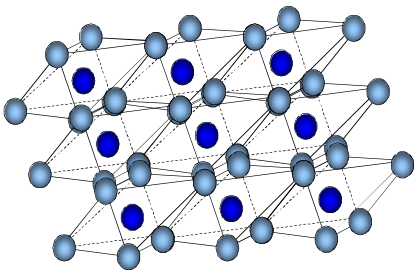
Chlorite (2:1:1) Nonexpanding

- Iron or Magnesium dominate most of the octahedral sites.
  - **Remember:** Al^{3+} usually dominates the octahedral sheet
- In most chlorite clays a magnesium-dominated octahedral sheet is sandwiched in between adjacent 2:1 layers.
- The hydroxides are hydrogen-bonded to the oxygen atoms of the two adjacent tetrahedral sheets, binding the layers tightly together.

Summary of Clay Structures



Óxidos de Fe, Al



Properties of Clays

TABLE 8.1 Major Properties of Selected Soil Colloids

Colloid	Type	Size, μm	Shape	Surface area, m^2/g: External	Surface area, m^2/g: Internal	Interlayer spacing[a], nm	Net charge[b], cmol/kg
Smectite	2:1 silicate	0.01–1.0	Flakes	80–150	550–650	1.0–2.0	−80 to −150
Vermiculite	2:1 silicate	0.1–0.5	Plates, flakes	70–120	600–700	1.0–1.5	−100 to −200
Fine mica	2:1 silicate	0.2–2.0	Flakes	70–175	—	1.0	−10 to −40
Chlorite	2:1 silicate	0.1–2.0	Variable	70–100	—	1.41	−10 to −40
Kaolinite	1:1 silicate	0.1–5.0	Hexagonal crystals	5–30	—	0.72	−1 to −15
Gibbsite	Al-oxide	<0.1	Hexagonal crystals	80–200	—	0.48	+10 to −5
Goethite	Fe-oxide	<0.1	Variable	100–300	—	0.42	+20 to −5
Allophane & Imogolite	Noncrystalline silicates	<0.1	Hollow spheres or tubes	100–1000	—	—	+20 to −150
Humus	Organic	0.1–1.0	Amorphous	Variable[c]	—	—	−100 to −500

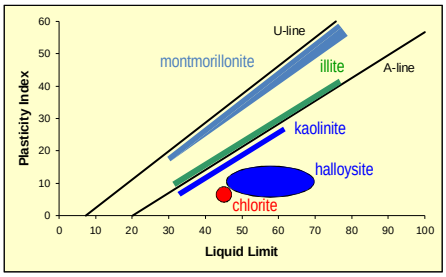
[a] From the top of one layer to the next similar layer, 1 nm = 10^{-9} m = 10 Å.
[b] Centimoles of charge per kilogram of colloid (cmol$_c$/kg), a measure of ion exchange capacity (see Section 8.9).
[c] It is very difficult to determine the surface area of organic matter. Different procedures give values ranging from 20 to 800 m^2/g.

Componente	Tipo de mineral	Fórmula química	Carga da camada	CTC ($cmol.kg^{-1}$)	ASE ($m^2 g^{-1}$)	Espaçamento (nm)	Expansividade	Dependência da carga com o pH	Atividade coloidal
Mica	2:1	$K_x[Al_2(Si_{4-x}Al_x)O_{10}(OH)_2]$	1,0	20-40	70-120	1,0	Não	Média	Alta
Vermiculita	2:1	$Na[Mg_3(Si_{4-x}Al_x)O_{10}(OH)_2]$	0,6-0,9	120-100	600-800	1,0-1,5	Não	Baixa	Alta
Montmorilonita	2:1	$Na_x(Al_{2-x}M_x)Si_4O_{10}(OH)_2$	0,25-0,6	80-120	600-800	Variável	Sim	Baixa	Extrem. alta
Clorita	2:1:1	$[AlMg_2(OH)_6]_x[Mg_3(Si_{4-x}Al_x)O_{10}(OH)_2]$	≈ 1	20-40	70-150	1,4	Não	Elevada	Média
Caulinita	1:1	$Al_2Si_2O_5(OH)_4$	≈ 0	1-10	10-20	0,72	Não	Elevada	Baixa
Alofana	-	$Si_xAl_y(OH)_{8-3y}$	-	10-150	70-300	-	-	Elevada	Média

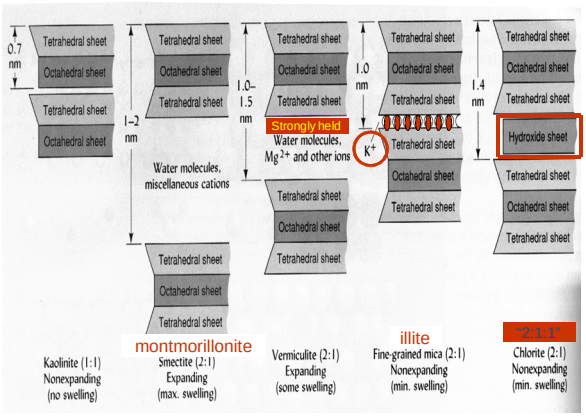
Properties of common silicate clays

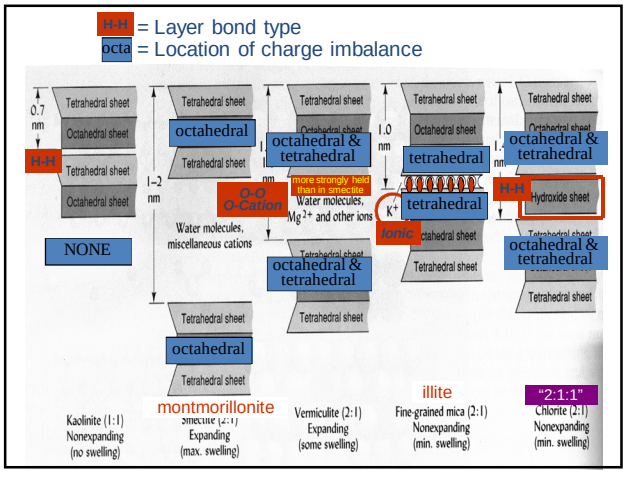
Property	Kaolinite	Smectites / Vermiculite	Illite (fine-grained micas)
General class	1:1 (TetraOcta)	2:1 (TOT)	2:1 (TOT)
Swelling	Low	**High**/Moderate	Low, none
Layer Bonding ionic > H-bonding > van der Waals	Hydrogen (strong)	O-O & O-Cation van der Waals (weak)	Potassium ions (strong)
Net negative charge (CEC) →Fertility	**Low**	**High / Highest**	Moderate
Charge location	**Edges** only – No isomorphic substitution	Octahedral / Octa+Tetra	Tetra(~balanced by K^+'s) so: Edges

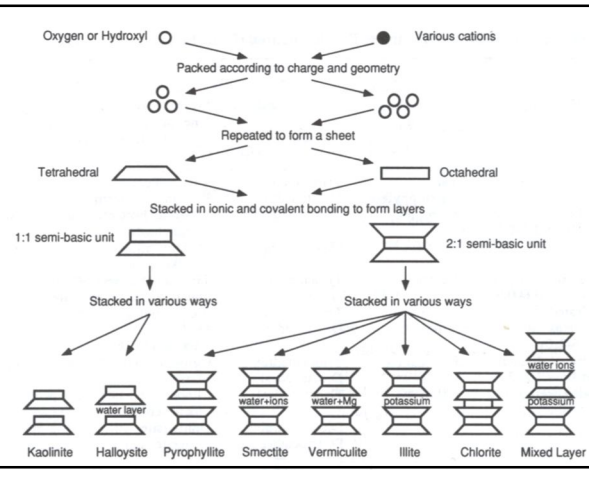
Casagrande's PI-LL Chart

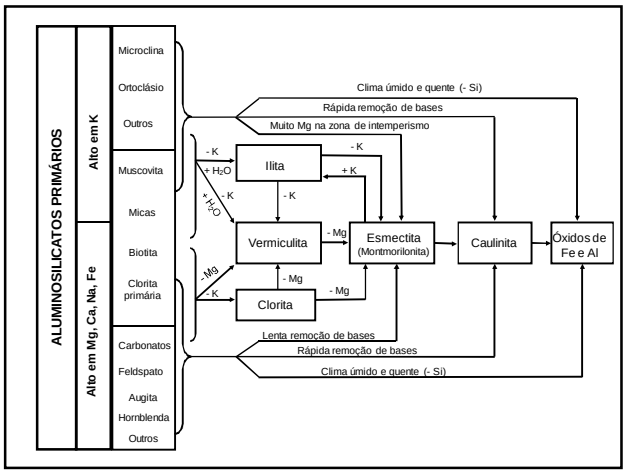


Visual comparison of common silicate clays





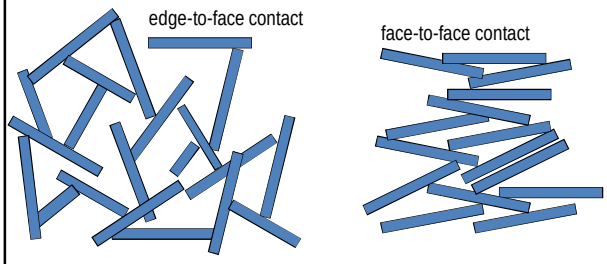




Clay Fabric

- Electrochemical environment (i.e., pH, acidity, temperature, cations present in the water) during the time of sedimentation influence clay fabric significantly.
- Clay particles tend to align perpendicular to the load applied on them.

Clay Fabric

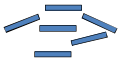


Flocculated *Dispersed*

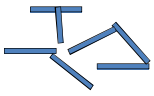
Types of Flocculation

1. Incomplete
2. Random
3. Plate Condensation

- Presence of dilute solution- weak or incomplete flocculation

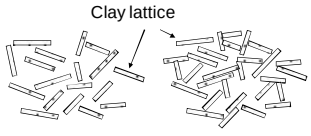


- Contact at the edges of clay plates



- Cations are aligned between two clay plates

Stability of clay suspension



High activity clays

Low activity clays

Greater distance between charged particles

kaolinite

montmorillonite, vermiculite

Fully hydrated clay particles are completely dispersed

Charge Properties of Clay minerals

Total charge on mineral surfaces is called intrinsic charge density or permanent charge

↓

Independent of soil reaction or pH

Variable charge is pH or proton dependent

↓

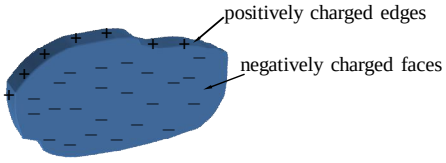
Imbalance of complex proton and hydroxyl charges on surface

Most soils have a net negative charge

Some weathered soils may have net positive

Isomorphous Substitution

- substitution of Si^{4+} and Al^{3+} by other lower valence (e.g., Mg^{2+}) cations
- results in charge imbalance (net negative)



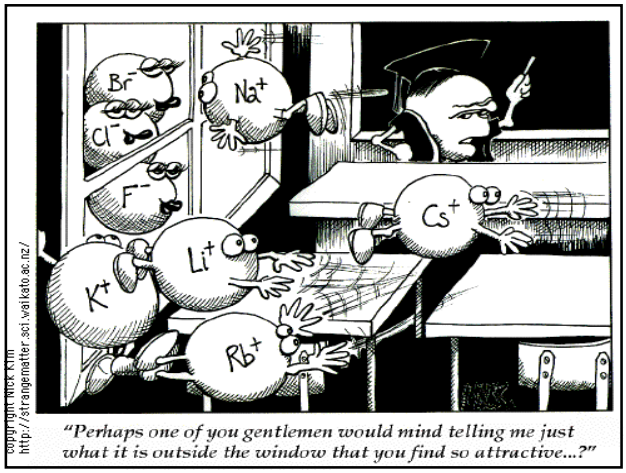
Clay Particle with Net negative Charge

What's so great about ion exchange?

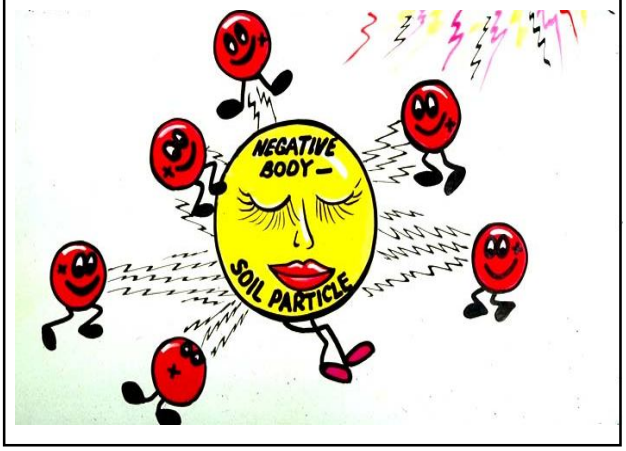
- Retards the release of pollutants to groundwater
- Affects permeability, with implications for landfills, ponds, etc.
- Affects nutrient availability to plants (constant supply, protection vs. leaching)

"Next to photosynthesis and respiration, probably no process in nature is as vital to plant and animal life as the exchange of ions between soil particles and growing plant roots."

Nyle C. Brady



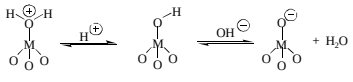
"Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive...?"



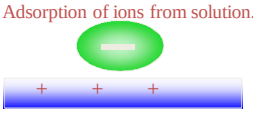
Origin of Surface Charge

Immersion of some materials in an electrolyte solution. Two mechanisms can operate.

(1) Dissociation of surface sites.

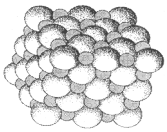


(2) Adsorption of ions from solution.

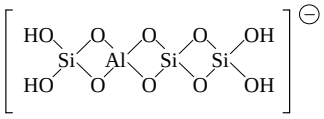


Origin of Surface Charge

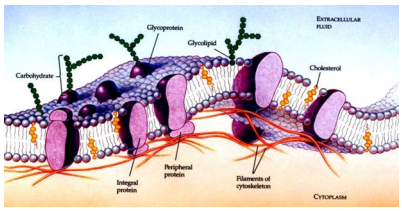
(3) Some ionic crystals have a slight imbalance in number of lattice cations or anions on surface, *eg.* AgI, $BaSO_4$, CaF_2,NaCl, KCl



(4) Surface charge due to crystal lattice defects, *eg.* lattice substitution in kaolin

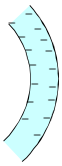


Other Surfaces with Charge



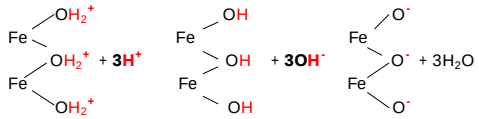
The bacteria membrane is made of a self organizing lipid bi-layer. Most of the lipids head-groups are negative charged.

Oil droplets develop negative charge.



Bubbles develop negative charge since cationic species are more mobile, than anionic species and accumulate to the interface.

Capacidade de Troca de Cátions - CTC
Capacidade de Troca de Ânions - CTA
Ponto de Carga Zero - PCZ



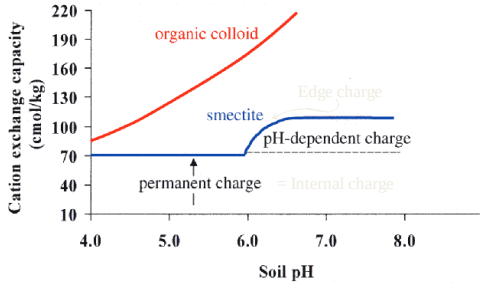
CTA $\Sigma- < \Sigma+$

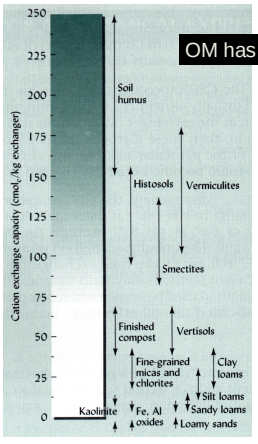
PCZ $\Sigma- = \Sigma+$

CTC $\Sigma- > \Sigma+$

PH aumenta

Influence of pH on the CEC of smectite and humus





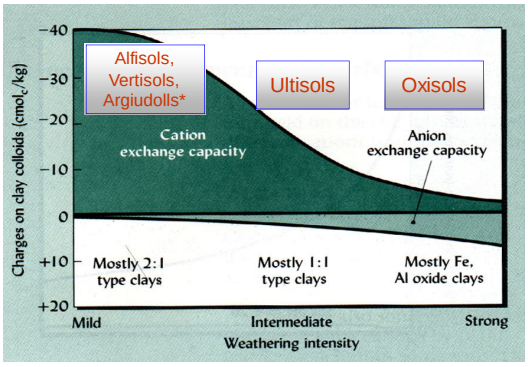
OM has highest CEC

2:1 clays

1:1 clays

Non-clayey soils

CEC and weathering intensity



*remember nomenclature structure = "argi-ud-oll"

Exchange affinity

Held more strongly — Held more weakly

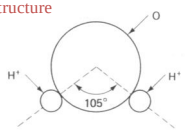
$$H^+ \geq Al^{3+} > Ca^{2+} > Mg^{2+} > NH_4^+ = K^+ > Na^+$$

This is referred to as the "Lyotropic series"

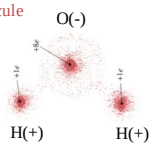
Strength of adsorption proportional to valence ÷ hydrated radius

Polar Water Molecules

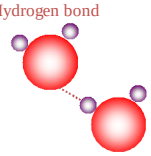
Structure



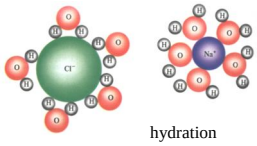
Polar molecule



Hydrogen bond



Salts in aqueous solution



hydration

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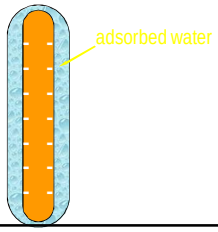
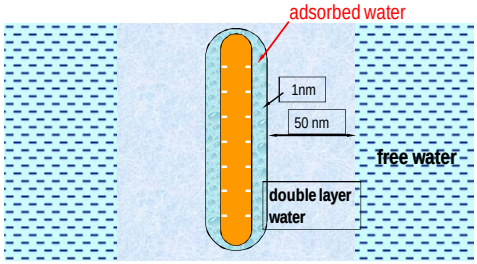
Adsorbed Water

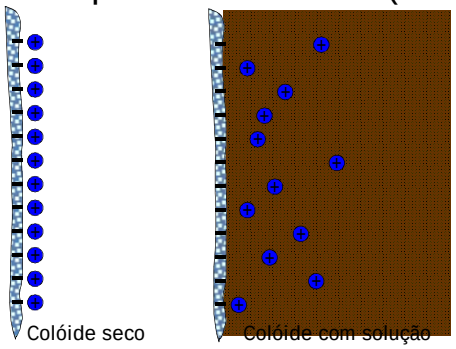
- A thin layer of water tightly held to particle; like a skin
- 1-4 molecules of water (1 nm) thick
- more viscous than free water



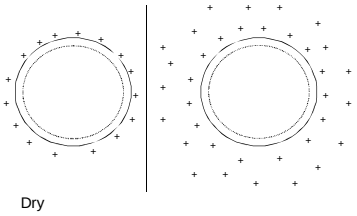
Clay Particle in Water



Dupla camada difusa (DDL)



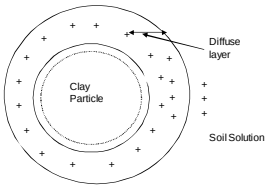
Electric double Layer



Negative charge on clay particles is balanced by the cations in soil solution (due to Coulomb forces).

Force that acts in two electrically charged bodies is proportional to the product of the module of their charges (q) divided by the square of the distance (*d*) between them

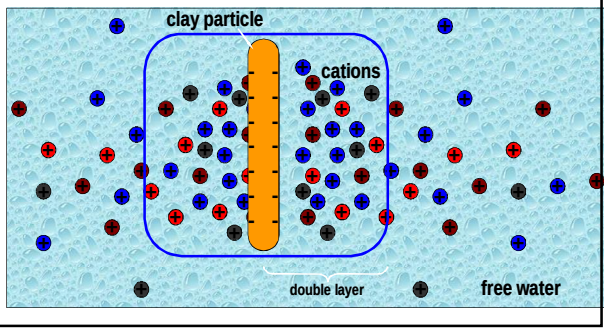
$$F = \frac{q_1 q_2}{d^2}$$



Electric double layer is due to the negative charge on clay particles and positive on surrounding cations in solution

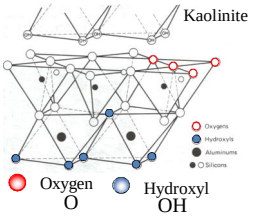
Cation Concentration in Water

- Cation concentration drops with distance from clay particle

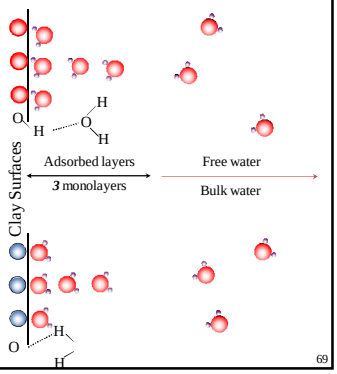


Clay-Water Interaction

1. Hydrogen bond



The water molecule "locked" in the adsorbed layers has different properties compared to that of the bulk water due to the strong attraction from the surface.



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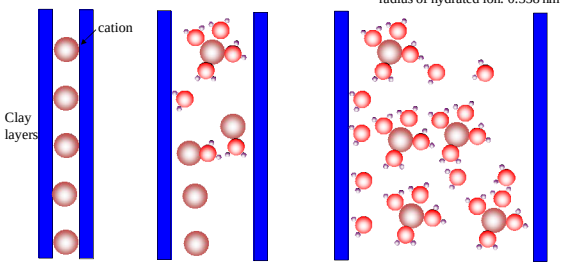
Clay-Water Interaction (Cont.)

2. Ion hydration

Na^+ crystal radius: 0.095 nm

radius of hydrated ion: 0.358 nm



Dry condition (Interlayer)

The water molecules wedge into the interlayer after adding water

The cations are fully hydrated, which results in repulsive forces and expanding clay layers (hydration energy).

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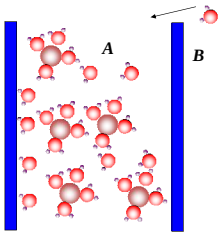
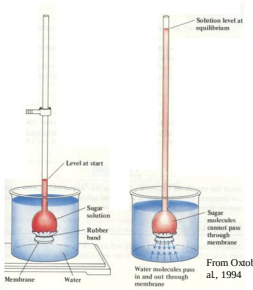
Clay-Water Interaction (Cont.)

3. Osmotic pressure





From Oxtoby et al., 1994

The concentration of cations is higher in the interlayers (A) compared with that in the solution (B) due to negatively charged surfaces. Because of this concentration difference, water molecules tend to diffuse toward the interlayer in an attempt to equalize concentration.

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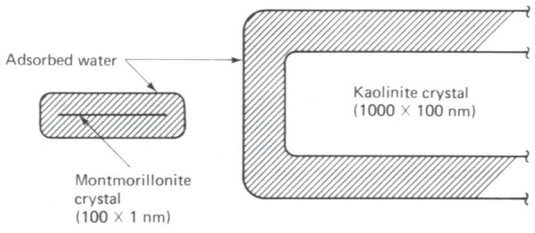
Clay-Water Interaction (Cont.)



Relative sizes of adsorbed water layers on sodium montmorillonite and sodium kaolinite

Holtz and Kovacs, 1981

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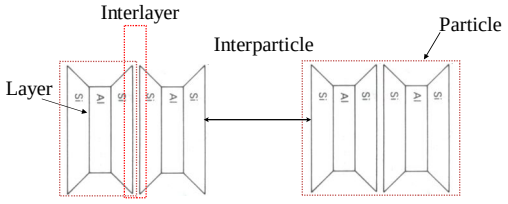
Interaction of Clay Particles (or Layers)



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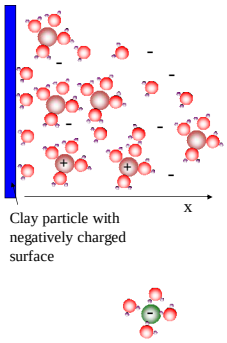
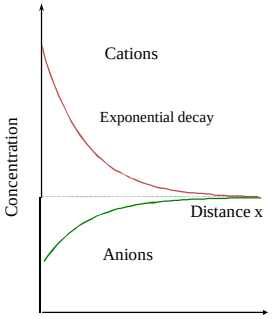
Diffuse Double Layer





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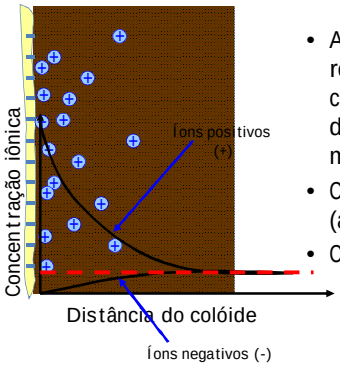
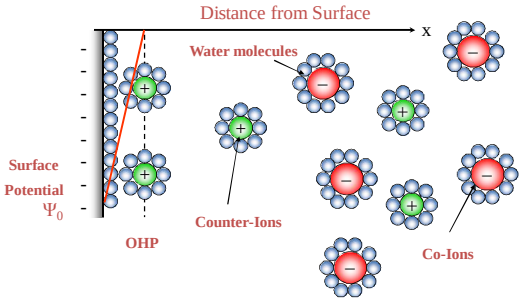
Estrutura da DDL



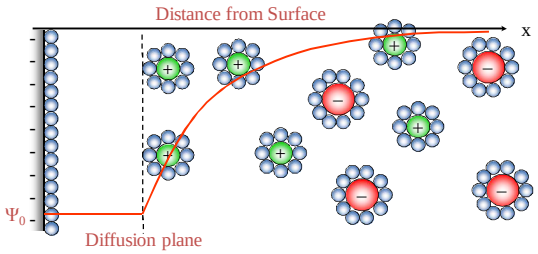
- A estrutura da DDL é resultante das forças competitivas entre forças de Coulomb e movimento Browniano
- Camada de Stern (adsorvido)
- Camada Difusa

Electrical Double Layer



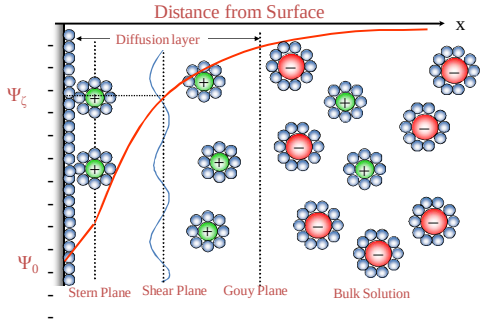
- Helmholtz (100+ years ago) proposed that surface charge is balanced by a layer of oppositely charged ions

Gouy-Chapman Model 1910-1913



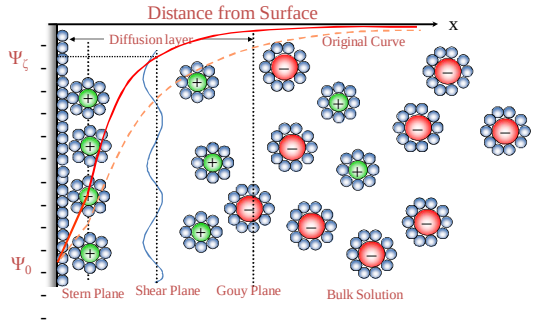
- Assumed Poisson-Boltzmann distribution of ions from surface
  - ions are point charges
  - ions do not interact with each other
- Assumed that diffuse layer begins at some distance from the surface

Stern (1924) / Grahame (1947) Model



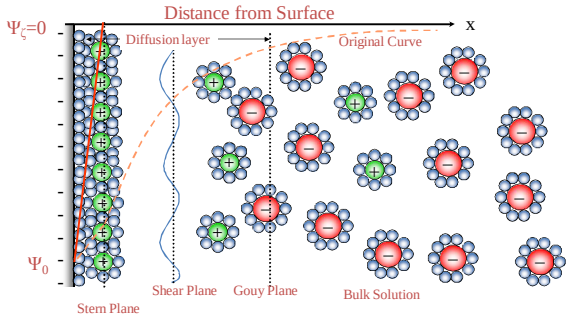
Gouy/Chapman diffuse double layer and layer of adsorbed charge

Salt Addition



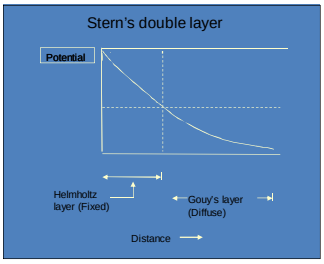
Salt will not effect the value of Ψ_0, but will effect the value of Ψ_ζ

Salt Addition



Further salt addition can collapse the EDL.

There are three models for explaining distribution of ion in water layer adjacent to clay

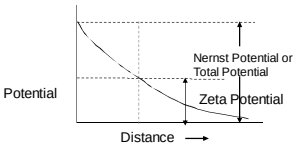


Helmholtz Model: All balancing cations are held in a fixed layer between the clay surface and soil solution

Gouy-Chapman Model: A diffuse double layer due to the thermal energy of cations causing a concentration gradient, which leads to a condition of maximum entropy or diffuse double layer

Stern Model: Combines the two concepts and proposes condition of free energy. Double layer comprises a rigid region next to mineral surface and a diffuse layer joining the bulk solution

Stern double layer comprises of two parts:
- single ion thick layer fixed to solid surface
- diffused layer extending some distance into liquid phase

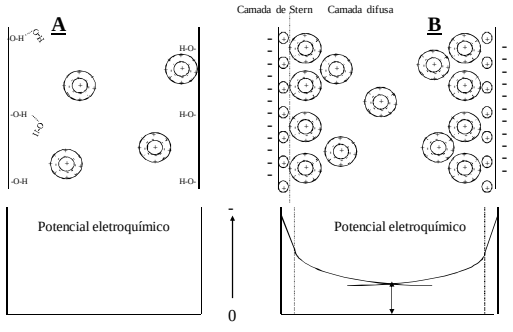


Thickness of double layer is the distance from the clay surface at which cation concentration reaches a uniform or minimum value

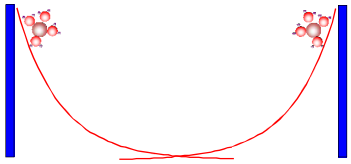
Zeta Potential: is the potential difference between the fixed and freely mobile diffuse double layer. It is also known as electrokinetic potential

Nernst Potential: is the difference in cross potentials at the interface of two phases when there is no mutual relative motion. It is also called thermodynamic or reversible potential

Comportamento da água e íons em (a) quartzo e (b) partícula de argila



Interaction Forces



Net force between clay particles (or interlayers)

DLVO forces
= van der Waals attraction +
Double layer repulsion (overlapping of the double layer)+
Coulombian attraction (between the positive edge and negative face)

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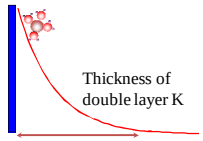
Thickness of Double Layer



$$K = \left(\frac{\varepsilon_0 \kappa \cdot kT}{2n_0 e^2 \nu^2}\right)^{1/2}$$

ε_0 : Permittivity in vacuum
κ : Relative permittivity
k : Boltzman constant
T : Temperature
n_0: Cation concentration
e : Electron charge
ν : Valence

K↑ repulsion force ↑

n_0↑ K↓ repulsion force ↓
ν↑ K↓ repulsion force ↓
T↑ K↑ repulsion force ↑(?)

κ decreases with increasing temperature

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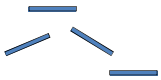
Interaction of Clay Particles

Dispersed fabric



The net interparticle force between surfaces is repulsive

Flocculated fabric

Edge-to-face (EF): positively charged edges and negatively charged surfaces (more common)

Edge-to-edge (EE)

Aggregated fabric

Face-to-Face (FF) ***Shifted FF***

Increasing	*Decreasing*	
Electrolyte concentration n_0	Permittivity κ	•Reduce the double layer repulsion (only applicable to some cases)
Ion valence ν	Size of hydration ion →	
Temperature T (?)	pH	•Flocculated or aggregated fabric
	Anion adsorption	

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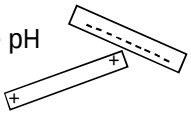
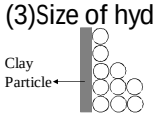
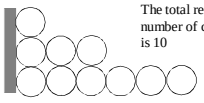
Interaction of Clay Particles (Cont.)

- (1) Decrease pH



- (2) Decrease anion adsorption
- (3)Size of hydration





The total required number of cations is 10

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Flocculation or Coagulation takes place once zeta potential is below the critical level

Sodium hexametaphosphate increases the zeta potential and suspension remains stable and does not coagulate

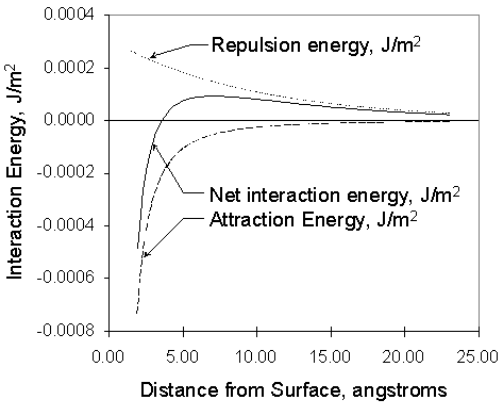
Effectiveness of a cation in causing flocculation depends on its valency

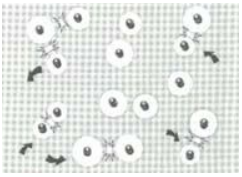
$H^+ > K^+ > Na^+ > Li^+$

$Ba^{+2} > Mg^{+2}$

$Al^{+3} > Ca^{+2} > Mg^{+2}$

Dispersivity increases in the opposite direction





Dispersed Particles

High Zeta Potential

Aggregated Particles

Low Zeta Potential

1. Almost all particulate or macroscopic materials in contact with a liquid acquire an electronic charge on their surfaces.
2. Zeta potential is an important and useful indicator of this charge which can be used to predict and control the stability of colloidal suspensions or emulsions.
3. The greater the zeta potential the more likely the suspension is to be stable because the charged particles repel one another and thus overcome the natural tendency to aggregate.
4. The measurement of zeta potential is often the key to understanding dispersion and aggregation processes
5. Zeta potential can also be a controlling parameter in processes such as adhesion, surface coating, filtration, lubrication and corrosion.

Flocculation or Coagulation: sticking together in clusters

Deflocculation or Dispersion- opposite

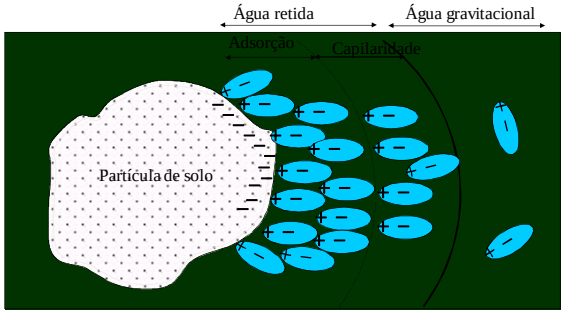
Chemically

Sodium Hexametaphosphate

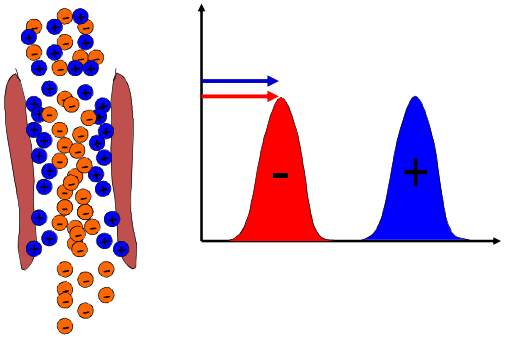
Mechanically

Stirring or Ultrasound vibration

Água e Íons



Efeito da DDL no transport → Retardamento



Próximo assunto:

Estrutura do solo