HIGH pH AND SALT AFFECTED SOILS

Assigned Reading: Sparks, Chapter 10.

Additional Reading McBride Chapter 8 (except 8.4c and 8.4d) Lindsay Chapter 6 and Agricultural Salinity Assessment and Management. ASCE. 1990. Chap. 3.

Carbonate Chemistry

Carbonates are Important in the Chemistry of Most High pH Soils

Equilibrium Solubility for the Carbonates of 2+ Metals

- **This involves solid--solution--gas phase equilibria.**
  - **Equilibrium is generally considered to be quite rapid relative to the alumino-silicates and hydrous oxides but slower than for gypsum and other evaporite minerals.**

Crystalline forms

- **Calcite** $CaCO_3$
- **Aragonite** $CaCO_3$
  - **A biogenic form slightly more soluble than calcite**
- **Dolomite** $CaMg(CO_3)_2$
  - **Forms very slowly in geological sediments**
- **Magnesite** $MgCO_3$
  - **More soluble than calcite**
- **Siderite** $FeCO_3$
  - **flooded soils**
- **Rhodochrosite** $MnCO_3$
  - **flooded soils - solid solution with siderite**

Carbonate species in water

- CO_2 in water: CO_2 + H_2O = $H_2CO_3^*$ $_{(aq)}$
  - —$H_2CO_3^*$
    - Includes both hydrated carbon dioxide molecules and carbonic acid.
      - Hydrated CO_2 is about 400x H_2CO_3.)
    - Is a function of the partial pressure of CO_2 (Pco_2) only. It is independent of pH.

Carbonate species in water (cont.)

- In ambient air, CO_2 is 0.00035 atm or 0.035%.
- Soil Pco_2 is elevated due to respiration by roots and microbes.
  - —0.003 to 0.2 atm
    - Highest in flooded soils.
      - The rate of movement of CO_2 (or any gas) through water is about 0.00001x that in the air.
      - When soils very wet gas exchange with the ambient air is slow

Calculation of [H_2CO_3*]

$CO_2 + H_2O = H_2CO_3^*$ log K = -1.46

log (H_2CO_3*) = -1.46 + log (P_{CO_2})

If P_{CO_2} = .0003 atm then

log (H_2CO_3*) = - 5.0
(increases linearly with P_{CO_2})

Basic Equations

	log K
1. $H_2O + CO_2 = H_2CO_3^*$	- 1.46
2. $H_2CO_3^* = H^+ + HCO_3^-$	- 6.35
3. $HCO_3^- = H^+ + CO_3^{2-}$	-10.33
4. $H_2O + CO_2 = H^+ + HCO_3^-$ (equation 1 and 2)	- 7.81
5. $H_2O + CO_2 = 2H^+ + CO_3^{2-}$ (equations 1,2, and 3)	-18.14
6. $H_2O = H^+ + OH^-$	-14.00 (K_w)
7. $CaCO_3 = Ca^{2+} + CO_3^{2-}$	- 8.48 to -8.35

Equilibrium Equations (cont.)

- **For some calculations we need the electroneutrality equation for the CO_2/H_2O system**

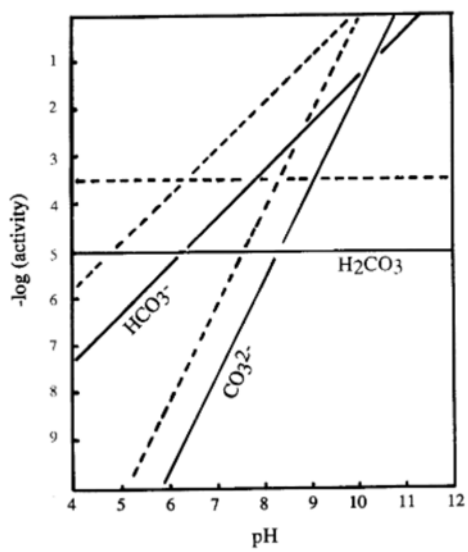
$[H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-]$ (8)

- **For some calculations we need the mass balance equation for carbon:**
- **$C_T = [H_2CO_3^*] + [CO_3^{2-}] + [HCO_3^-]$ (9)**
    - **C_T = Dissolved Inorganic Carbon (DIC)**

Equilibrium Equations (cont.)

- **These equations can be used to express species in terms of other species e.g. $H_2CO_3^*$ and CO_3^{2-} can be expressed in terms of HCO_3^- and H^+.**
- **In soils and natural waters with pH 5.5 - 9.5, HCO_3^- is a very important anion.**
- **In low pH soils, organic anions and SO_4^{2-} become relatively more important.**
- **CO_3^{2-} is important only in very alkaline soils.**

Activity of dissolved inorganic C species at log P_{CO2} = -3.5 and -2.0 (Fig 8.2)



CO_2 in water with no Carbonate Solids

- **Alkalinity**

Alk = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$ + titratable organic anions

- **Alkalinity is normally determined by titration with acid to pH 4.8 (pH at which all DIC is in the form of H_2CO_3*).**
  - **In MINTEQ Alk is given in $cmol_cL^{-1}$**
    Alk = $[HCO_3^-] + 2[CO_3^{2-}]$
- **In the range of 5.6-9.5 alkalinity is primarily due to HCO_3^-.**

Effect of pH and P_{CO2} on $[HCO_3^-]$ and $[CO_3^{2-}]$

- From equations 1 & 2 we get equation

$H_2O + CO_2 = H^+ + HCO_3^-$ log K = -7.81

log (HCO_3^-) = pH + log Pco_2 - 7.81 (10)

$$K = \frac{(H^+)(HCO_3^-)}{P_{CO_2}}$$

Effect of pH and P_{CO2} on $[HCO_3^-]$ and $[CO_3^{2-}]$ (cont.)

- On a log (HCO_3^-) vs. pH plot the slope = +1
- From equations 1, 2, and 3 we get equation 5 (see McBride Fig. 8.2)

$H_2O + CO_2 = 2H^+ + CO_3^{2-}$ log K = -18.14

- From the equilibrium constant expressions
  - log (CO_3^{2-}) = 2pH + log Pco_2 - 18.14
- On a log (CO_3^{2-}) vs. pH plot the slope = +2

Effect of pH and P_{CO2} on $[HCO_3^-]$ and $[CO_3^{2-}]$ (cont.)

– Example: pH = 7.0, Pco_2 = 0.0050 atm

- $\log (HCO_2^-) = 7.0 - 2.3 - 7.81$

  $\log (HCO_2^-) = -3.1$

- $\log (CO_3^{2-}) = 2(7.0) - 2.3 - 18.14$

  $\text{Log } (CO_3^{2-}) = -6.44$

Review of Basic Equations

	log K
1. $H_2O + CO_2 = H_2CO_3^*$	- 1.46
2. $H_2CO_3^* = H^+ + HCO_3^-$	- 6.35
3. $HCO_3^- = H^+ + CO_3^{2-}$	-10.33
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Dissolution of Calcite

- **Combining eqn. 7 with eqn. 5.**

$CaCO_3 + 2H^+ = H_2O + CO_2 + Ca^{2+}$ log K = 9.66 (11)

- **Write the equilibrium constant then take the log of both sides.**
  - **$9.79 = \log Pco_2 + \log Ca^{2+} + 2\ pH$ (12)**
  - **$\log [Ca^{2+}] = 9.79 - \log Pco_2 - 2pH$**

- **Fixed $[Ca^{2+}]$**
  - **e.g. Fix(Ca^{2+}) at 0.010 <u>M</u>, $Pco_2 = 10^{-3.5}$**
    - **pH = 7.6**

pH in Equilibrium with Calcite and No other Acidity or Alkalinity

- **Species Ca^{2+}, H_2CO_3*, HCO_3^-, H^+, CO_3^{2-}, OH^-**
- **Use eqns. 1, 2, 3, 6, 7 plus the charge balance.**
- **Charge balance**

$2[Ca^{2+}] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$ (13)

pH in Equilibrium with Calcite (cont)

- **At the pH of the equilibrium system**
  - **$[H^+]$, $[CO_3^{2-}]$, and $[OH^-] \approx 0$**
  - **Thus the charge balance is $2[Ca^{2+}] \approx [HCO_3^-]$**
  - **Use eqn.10 to calculate $[HCO_3^-]$ assuming $g_{HCO3} = 1$, and substitute for $[HCO_3^-]$ using equation 13.**
  - **Then (14)**

$$2[Ca^{2+}] = \frac{\left(10^{-7.81}\right)\left(P_{CO_2}\right)}{[H^+]}$$

pH in Equilibrium with Calcite (cont)

- **Taking the log of both sides**

  $\log [Ca^{2+}] = -8.11 + \log Pco_2 + pH$
- **equate to eqn. 12**

  $-8.11 + \log Pco_2 + pH = 9.79 - \log Pco_2 - 2pH$

  $3\ pH = 17.90 - 2 \log Pco_2$
- **pH is a function of Pco_2, only.**
  - **If $Pco_2 = 10^{-3.5}$, pH = 8.3**
    - **This is often the reference pH for potential CEC.**
  - **If $Pco_2 = 10^{-2.5}$, pH = 7.6**

Equilibrium with Calcite (cont.)

- **Calculate the Ca^{2+} concentration using equation 12 and the HCO_3^- concentration using equation 10 or the charge balance**

  —**for $P_{CO_2} = 10^{-3.5}$, $[Ca^{2+}] = 5.0 \times 10^{-4}$M**
  —**for $P_{CO_2} = 10^{-2.5}$, $[Ca^{2+}] = 1.2 \times 10^{-3}$M**

pH in Equilibrium with Calcite (cont.)

- **In most soils $2[Ca^{2+}]$ does not equal $[HCO_3^-]$**
  - **If $[Ca^{2+}] = 0.010$ M and $P_{CO_2} = 0.005$, then $2[Ca^{2+}] > [HCO_3^-]$**
  - **From . 12, pH = 7.05.**
  - **From equation 10. $[HCO_3^-] = 1.0 \times 10^{-3}$ M and anions other than bicarbonate make up most of the anionic charge.**
  - **In soils with Ca controlled by gypsum $[Ca^{2+}] > 0.01$ M.**

pH with calcite and added alkalinity

- **Soils containing bicarbonate of Na^+ and Mg^{2+} and $2[Ca^{2+}]$ is $<[HCO_3^-]$**
  - **If $[HCO_3^-] = 0.010$ M and $Pco_2 = 0.005$**
    - **From equation 10 pH = 8.05**
    - **from eqn. 12, and $[Ca^{2+}] = 1.0 \times 10^{-4}$ M**

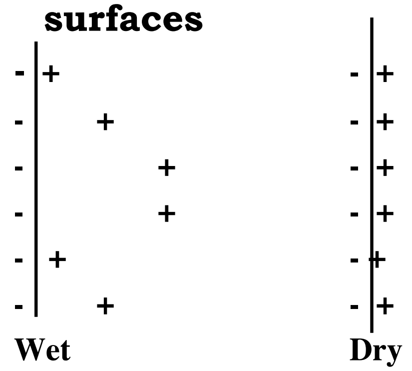
SWELLING AND DISPERSION OF CHARGED PARTICLES IN SOILS

Charged surfaces

- Charged Surfaces
  - pH dependent
    - hydrous oxides
    - silicate clay edges
    - organic matter

Example: Permanent Charge Clays

- Monovalent cations near charged surfaces



Diffuse double layer thickness (DDL)

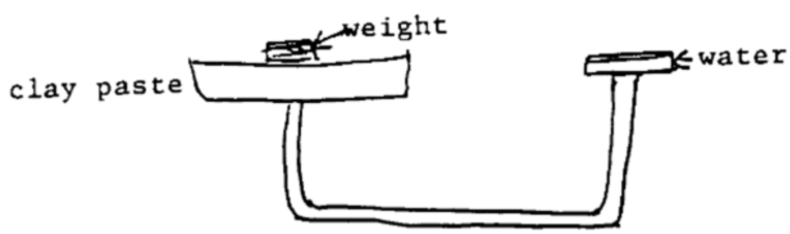
- **DDL is a function of C_o and *z* of cation.**
  - **Example: 10^{-3} mol L^{-1} NaCl**
    - **DDL for smectite ≈ 20 nm**
  - **Increasing salt concentration reduces DDL and hence reduces swelling pressure**
    - **In Ca^{2+}, less than 10 Å**
    - **Tactoid formation**

Diffuse double layer thickness (cont.)

- **Swelling of Clays**
  - **Monovalent cations**
    - **At low ionic strength platelets are at the maximum distance apart.**
    - **Divalent and trivalent**
      - **Tactoid formation**

Free swelling of a clay paste

- **Soil moisture tension = 0**



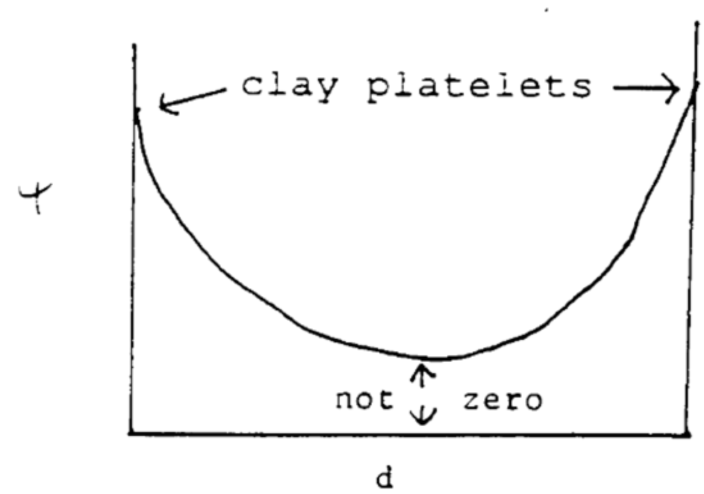
Free swelling of a clay paste (cont)

Table 8.3. Swelling Volumes of Metal-Exchanged Smectites in Water (cm^3/g)

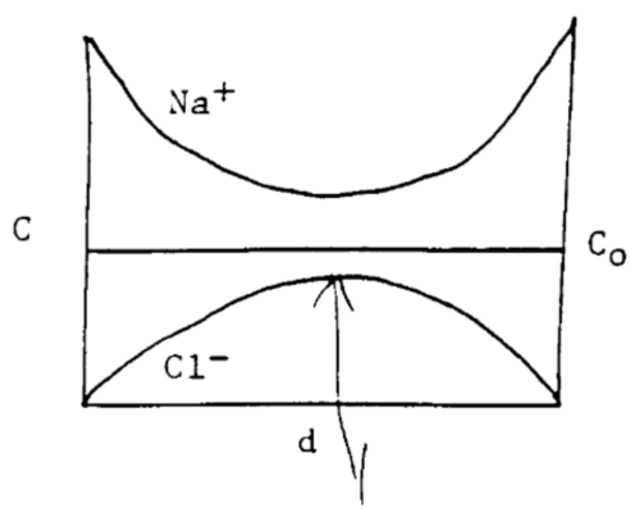
H^+	Li^+	Na^+	K^+	Ca^{2+}	Ba^{2+}
(2.20)[a]	10.8	11.1	8.6	2.5	2.5

[a]Clay has probably decomposed to the Al^{3+}-saturated form.

Potential (volts) that cases swelling

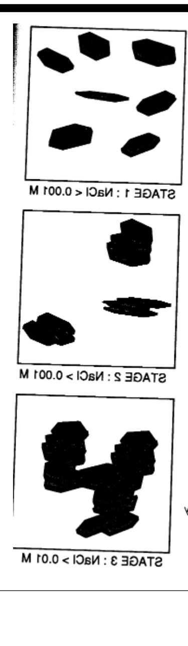


Concentration of NaCl between clay platelets with a positive swelling pressure

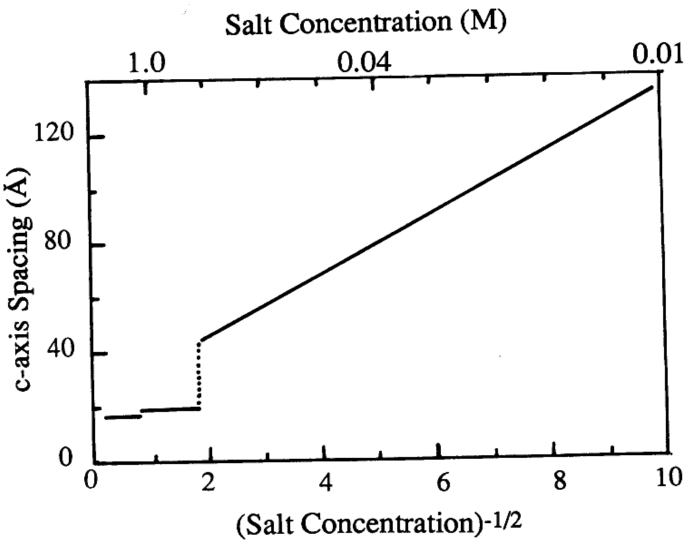


- **Increasing salt concentration reduces DDL thickness and hence reduces swelling pressure**

Aggregation of smectites with increasing salt concentration (McBride Fig 8.6)



Effect of NaCl concentration on interlayer swelling (Fig. 8-7)



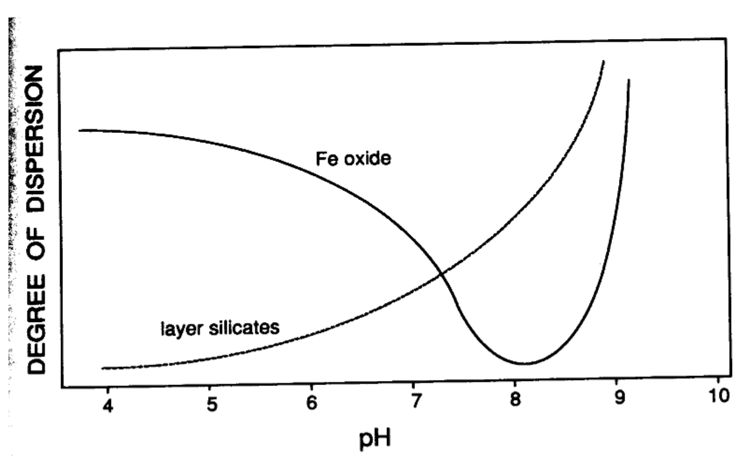
Flocculation

- **High salt concentration**
- **High charge cations**
- **With monovalent ions the critical concentration for coagulation (CCC)of smectite clay is high. (0.025-0.150 M)**
- **With multicharge ions the CCC is low. (0.0005-0.002 M for M^{2+}; 1 x 10^{-5} - 1 x 10^{-4} M for M^{3+})**

Flocculation (cont.)

- **For pH dependent charge minerals**
  - **Flocculation at high CCC values or at pznc**
- **Divalent and higher charge ions that form surface complexes which neutralize charge and can produce cation bridges with organic matter .**
  - **This causes flocculation even at low concentrations (low CCC)**

Effect of pH on dispersion of iron oxide



SODICITY AND SALINITY IN ARID REGION SOILS

Definitions

- **Saline soil = high salts**
- **Sodic soil = high Na**

Extent of Agricultural Salt Problems

- **United States**
  - **About 30% of the land has a moderate to severe potential for saline-sodic problems.**
  - **Western states have a high potential for problems with salinity/sodicity.**
  - **Example: California:**
    - **1,720,000 ha are saline or sodic**
    - **1,100,000 ha have a water table at a depth of 1.5 m or less.**
    - **1,400,000 ha have problems with water quality.**

Measures of salinity and alkalinity(connect to water quality)

- **Residual Sodium Carbonate (RSC)**
  - **Measure excess alkalinity in irrigation water**

    RSC = $[HCO_3^- + CO_3^{2-}] - [Ca^{2+} + Mg^{2+}]$
    - **RSC = the acidity ($mmoles_v\ L^{-1}$) that is needed to neutralize the solution alkalinity in excess of the alkalinity associated with Ca and Mg.**
    - **Titrate to pH = 4.8**
  - **Any excess of CO_3^{2-} or HCO_3^- not precipitated by Mg or Ca during evaporation in soils is alkalinity hazard and can result in high pH values soil**

RSC > 2.5 (mmole L^{-1})	Hazardous
RSC = 1.25 - 2.5	Potentially hazardous
RSC < 1.25	Generally safe

Salinity Hazard

- Electrical Conductivity (EC)
  - Principles
    - Conductivity is the ease with which an electric current is carried through a solution
    - Conductivity is proportional to the quantity of ions (quantity of ionic charge) in solution.
- Electrical conductance
  - Reciprocal of electrical resistance
    - ohms ($ohms^{-1}$), mho
    - Now defined as Siemen (1 Siemen = 1 mho)

Electrical conductivity (EC)

- EC = Conductance(Siemens) x distance (cm)÷ area (cm^2)

- Units: S/cm = mho cm^{-1}.
  - mho cm^{-1} is too large soil solutions
  - Use mmho cm^{-1} = mS cm^{-1}= dS m^{-1}
  - Soil scientist generally use dS m^{-1}
  - McBride uses mS cm^{-1}

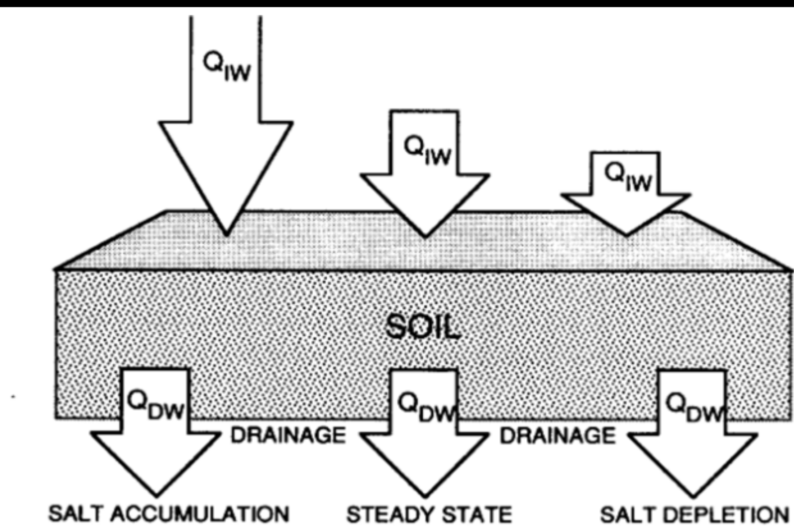
EC of saturated soil paste

- In the US soil salinity is usually determined by EC of saturated paste extracts.
  - Distilled water is added to dried soil until is is at the saturation limit,
  - Them EC is measured on the extracted solution.

EC of saturated soil paste (cont.)

- Plants vary in response to salt
  - EC values over 2 dS m^{-1} (m mho cm^{-1}) suggests potential for problems
  - Value > 4 means that only tolerant plants will survive.
- 1:1 Soil extracts are also used.
  - Different interpretations are needed.

Accumulation of salts in irrigated soils (Fig.8-22)



Use of Ion Exchange Theory to predict the long-term effect of irrigation water on soils

- **Vanselow equation**
  - **Vanselow selectivity coefficient is used in California and by some investigators outside of CA.**
  - **Most use Gapon**
- **Gapon equation**

  $Ca_{1/2}X + 2Na^{+} = 2NaX + 1/2Ca$

Gapon Equation

- **Mg^{2+} and Ca^{2+} are considered as one ion**

$$K_G = \frac{N_{Na}[[Ca^{2+}] + [Mg^{2+}]]^{\frac{1}{2}}}{N_{Ca+Mg}[Na^{+}]}$$

- **K = 0.015 if solution concentrations are in mmol L^{-1}**

Gapon Equation (cont.)

- **With long-term addition of irrigation water the soil will be in equilibrium with the water.**
- **Can predict the equilibrium $N_{Na\ \#}$ (charge fraction of Na on the soil particles)**
- **With high Na on the exchange sites the soil particles can disperse.**

Gapon Equation (cont.)

$$\frac{N_{Na}}{N_{Ca+Mg}} = K_G \frac{[Na^+]}{[[Ca^{2+}] + [Mg^{2+}]]^{\frac{1}{2}}}$$

$$\frac{N_{Na}}{N_{Ca+Mg}} = \left(\frac{NaX}{CEC - NaX}\right) = K_G SAR$$

SAR: Sodium Adsorption Ratio

- **An irrigation water term**

$$SAR = \frac{[Na^{+}]}{[[Ca^{2+}]+[Mg^{2+}]]^{\frac{1}{2}}}$$

Exchangeable Sodium Ratio (ESR)

- **ESR: Exchangeable Sodium Ratio (a soil term)**

$$\frac{N_{Na}}{N_{Ca+Mg}} = ESR$$

ESR = K_G(SAR)

Exchangeable Sodium Percentage (ESP) (a soil term)

- ESR is the equilibrium fraction of Na on exchange sites expressed as a percentage.

$$\left(\frac{NaX}{CEC}\right) \cdot 100 = ESP$$

$$\frac{ESP}{100 - ESP} = ESR = K_G SAR$$

Soil structure stability

- Role of salinity and sodicity in swelling and dispersion
  - Clay swelling enables individual platelets to separate and form a stable dispersion
- This swelling can be suppressed by high salt concentration
- Multivalent exchange cations, Ca, Mg, Al, counteract swelling by forming electrostatic bridges between adjacent platelets (platelets stack), "quasi-crystals"

Soil structure stability (cont.)

- The Na/(Ca+Mg) ratio controls particle size, arrangement, and dispersibility.

- As ESP increases, soil aggregate structure deteriorates. This causes reduced permeability and drainage, poor aeration, surface crusting and shrink-swell under cycles of wetting and drying.

Traditional Classification of Salinity and Sodicity

ESP%

pH > 9 Sodic Poor Dispersed	pH < 8.5 Saline-sodic Fair-good Flocculated
pH < 8.5 NORMAL	pH<8.5 Saline Good Flocculated

15%

4 dSm^{-1}

Brief Summary

- The chemistry of dissolved inorganic carbon (DIC) is important in soils.
- Alkalinity in most soils is mostly bicarbonate.
- High pH soils generally contain calcite
  - Calcite buffers the pH in high pH soils.
- Soil clays and OM can disperse in Na^+, Li^+, and K^+.
  - The dispersion is the result of the surface potential and the double layer effects

Brief Summary (cont.)

- Double layer thickness decreases at high salt concentrations.
- Smectites form tactoids in divalent salts and easily flocculate.
- The effects of long-term of irrigation water application on Na^+ saturation in soils can be predicted by the Gapon ion exchange equation
- Salinity is measured by EC.
- The EC of soil pastes or 1:1 suspensions is used to predict salinity hazard in soils.