
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** $\text{CaMg}(\text{CO}_3)_2$
 - **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

- **CO₂ in water: CO₂ + H₂O = H₂CO₃* (aq)**

—H₂CO₃*

- **Includes both hydrated carbon dioxide molecules and carbonic acid.**
 - Hydrated CO₂ is about 400x H₂CO₃.)
- **Is a function of the partial pressure of CO₂ (Pco₂) only. It is independent of pH.**

Carbonate species in water (cont.)

- **In ambient air, CO₂ is 0.00035 atm or 0.035%.**
- **Soil Pco₂ is elevated due to respiration by roots and microbes.**
 - **0.003 to 0.2 atm**
 - **Highest in flooded soils.**
 - **The rate of movement of CO₂ (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 $[H_2CO_3^*]$



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

If $P_{CO_2} = .0003$ atm then

$$\log (H_2CO_3^*) = -5.0$$

(increases linearly with P_{CO_2})

Basic Equations

	<u>log K</u>
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 CO₂/H₂O system**

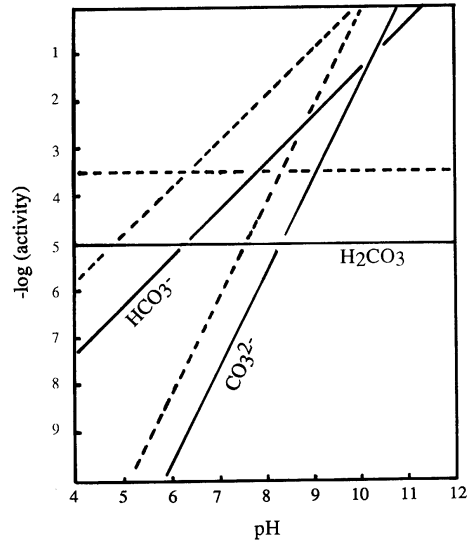
$$[\text{H}^+] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] \quad (8)$$

- **For some calculations we need the mass balance equation for carbon:**
- **C_T = [H₂CO₃*] + [CO₃²⁻] + [HCO₃⁻] (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. H₂CO₃* and CO₃²⁻ can be expressed in terms of HCO₃⁻ and H⁺.**
- **In soils and natural waters with pH 5.5 - 9.5, HCO₃⁻ is a very important anion.**
- **In low pH soils, organic anions and SO₄²⁻ become relatively more important.**
- **CO₃²⁻ 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)**



**CO₂ in water with no Carbonate
Solids**

• **Alkalinity**

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + \text{titratable organic anions}$$

– Alkalinity is normally determined by titration with acid to pH 4.8 (pH at which all DIC is in the form of H₂CO₃*).

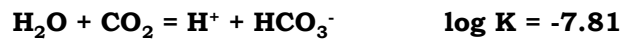
• In MINTEQ Alk is given in cmol_cL⁻¹

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

– In the range of 5.6-9.5 alkalinity is primarily due to HCO₃⁻.

Effect of pH and P_{CO_2} on $[HCO_3^-]$ and $[CO_3^{2-}]$

- From equations 1 & 2 we get equation



$$\log (HCO_3^-) = \text{pH} + \log P_{CO_2} - 7.81 \quad (10)$$

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

Effect of pH and P_{CO_2} 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)



—From the equilibrium constant expressions

- $\log (CO_3^{2-}) = 2\text{pH} + \log P_{CO_2} - 18.14$

—On a log (CO_3^{2-}) vs. pH plot the slope = +2

Effect of pH and P_{CO_2} on $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ (cont.)

—Example: pH = 7.0, $P_{\text{CO}_2} = 0.0050$ atm

$$\bullet \log (\text{HCO}_3^-) = 7.0 - 2.3 - 7.81$$

$$\log (\text{HCO}_3^-) = -3.1$$

$$\bullet \log (\text{CO}_3^{2-}) = 2(7.0) - 2.3 - 18.14$$

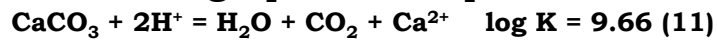
$$\text{Log} (\text{CO}_3^{2-}) = -6.44$$

Review of Basic Equations

	<u>log K</u>
1. $\text{H}_2\text{O} + \text{CO}_2 = \text{H}_2\text{CO}_3^*$	- 1.46
2. $\text{H}_2\text{CO}_3^* = \text{H}^+ + \text{HCO}_3^-$	- 6.35
3. $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	-10.33
4. $\text{H}_2\text{O} + \text{CO}_2 = \text{H}^+ + \text{HCO}_3^-$ (equation 1 and 2)	- 7.81
5. $\text{H}_2\text{O} + \text{CO}_2 = 2\text{H}^+ + \text{CO}_3^{2-}$ (equations 1,2, and 3)	-18.14
6. $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	-14.00 (K_w)
7. $\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	- 8.48 to -8.35

Dissolution of Calcite

- Combining eqn. 7 with eqn. 5.



- Write the equilibrium constant then take the log of both sides.

$$9.79 = \log P_{\text{CO}_2} + \log [\text{Ca}^{2+}] + 2 \text{pH} \quad (12)$$

$$\log [\text{Ca}^{2+}] = 9.79 - \log P_{\text{CO}_2} - 2\text{pH}$$

- Fixed $[\text{Ca}^{2+}]$

– e.g. Fix(Ca^{2+}) at 0.010 M, $P_{\text{CO}_2} = 10^{-3.5}$

- $\text{pH} = 7.6$

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

$$2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (13)$$

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 $\alpha_{HCO_3} = 1$, and substitute for $[HCO_3^-]$ using equation 13.
 - Then (14)

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

pH in Equilibrium with Calcite (cont)

- Taking the log of both sides

$$\log [Ca^{2+}] = -8.11 + \log P_{CO_2} + pH$$
- equate to eqn. 12

$$-8.11 + \log P_{CO_2} + pH = 9.79 - \log P_{CO_2} - 2pH$$

$$3 pH = 17.90 - 2 \log P_{CO_2}$$
- pH is a function of P_{CO_2} , only.
 - If $P_{CO_2} = 10^{-3.5}$, $pH = 8.3$
 - This is often the reference pH for potential CEC.
 - If $P_{CO_2} = 10^{-2.5}$, $pH = 7.6$

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 $\text{Pco}_2 = 10^{-3.5}$, $[\text{Ca}^{2+}] = 5.0 \times 10^{-4} \text{M}$

—for $\text{Pco}_2 = 10^{-2.5}$, $[\text{Ca}^{2+}] = 1.2 \times 10^{-3} \text{M}$

pH in Equilibrium with Calcite (cont.)

- **In most soils $2[\text{Ca}^{2+}]$ does not equal $[\text{HCO}_3^-]$**
 - **If $[\text{Ca}^{2+}] = 0.010 \text{ M}$ and $\text{Pco}_2 = 0.005$, then $2[\text{Ca}^{2+}] > [\text{HCO}_3^-]$**
 - **From . 12, $\text{pH} = 7.05$.**
 - **From equation 10. $[\text{HCO}_3^-] = 1.0 \times 10^{-3} \text{ M}$ and anions other than bicarbonate make up most of the anionic charge.**
 - **In soils with Ca controlled by gypsum $[\text{Ca}^{2+}] > 0.01 \text{ M}$.**

pH with calcite and added alkalinity

- **Soils containing bicarbonate of Na^+ and Mg^{2+} and $2[\text{Ca}^{2+}]$ is $<[\text{HCO}_3^-]$**

—If $[\text{HCO}_3^-] = 0.010 \text{ M}$ and $P_{\text{CO}_2} = 0.005$

- **From equation 10 $\text{pH} = 8.05$**
- **from eqn. 12, and $[\text{Ca}^{2+}] = 1.0 \times 10^{-4} \text{ M}$**

SWELLING AND DISPERSION OF CHARGED PARTICLES IN SOILS

Diffuse double layer thickness (DDL)

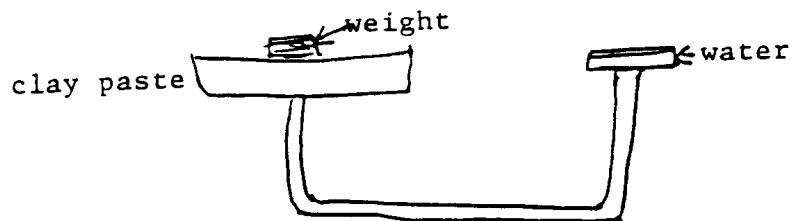
- **DDL is a function of C_0 and z of cation.**
 - **Example: $10^{-3} \text{ mol L}^{-1} \text{ NaCl}$**
 - **DDL for smectite $\approx 20 \text{ nm}$**
 - **Increasing salt concentration reduces DDL and hence reduces swelling pressure**
 - **In Ca^{2+} , less than 10 \AA**
 - **Tactoid formation**

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



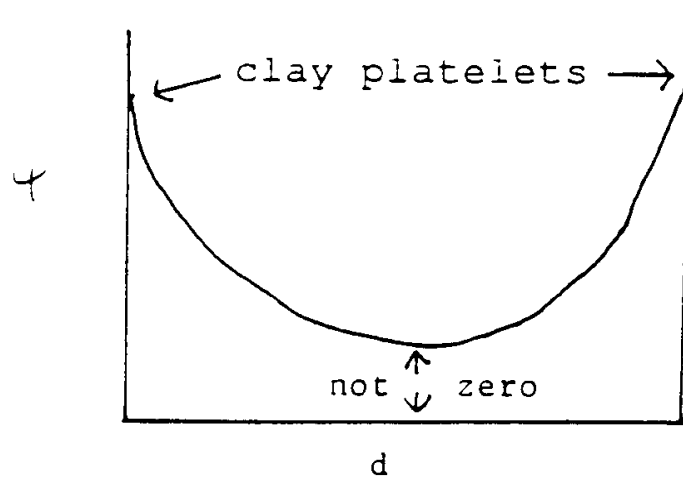
Free swelling of a clay paste (cont)

Table 8.3. Swelling Volumes of Metal-Exchanged Smectites in Water (cm³/g)

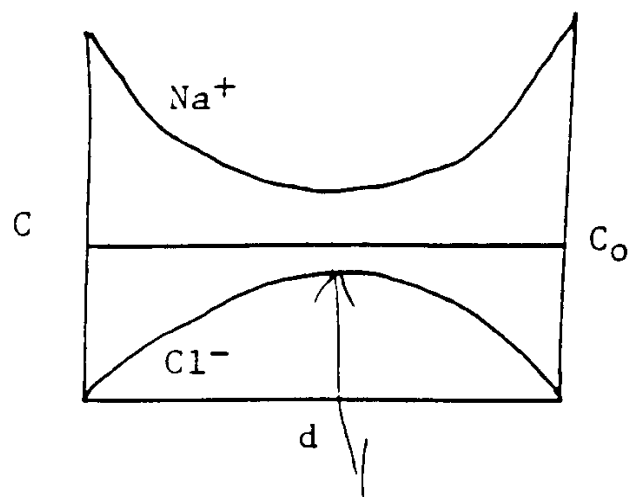
H ⁺	Li ⁺	Na ⁺	K ⁺	Ca ²⁺	Ba ²⁺
(2.20) ^a	10.8	11.1	8.6	2.5	2.5

^aClay has probably decomposed to the Al³⁺-saturated form.

Potential (volts) that causes swelling

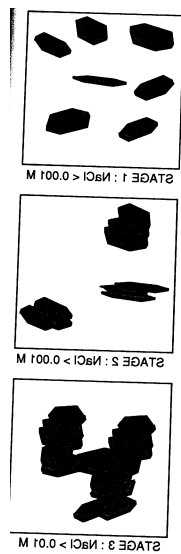


Concentration of NaCl between clay platelets with a positive swelling pressure

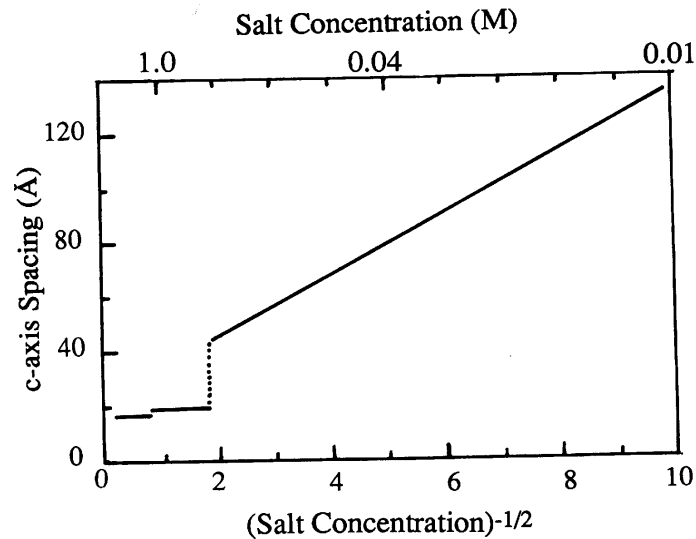


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- **Increasing salt concentration reduces DDL thickness and hence reduces swelling pressure**

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



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



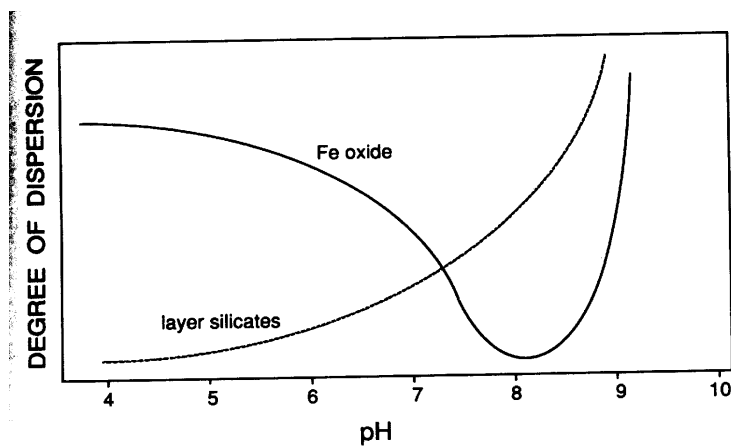
Flocculation

- **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 M²⁺; 1 x 10⁻⁵ - 1 x 10⁻⁴ M for M³⁺)**

Flocculation (cont.)

- **For pH dependent charge minerals**
 - Flocculation at high CCC values or at p_{znc}
- **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**

$$\text{RSC} = [\text{HCO}_3^- + \text{CO}_3^{2-}] - [\text{Ca}^{2+} + \text{Mg}^{2+}]$$

- **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 CO₃²⁻ or HCO₃⁻ 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 hazardous	Potentially
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 (cm²)**
- **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

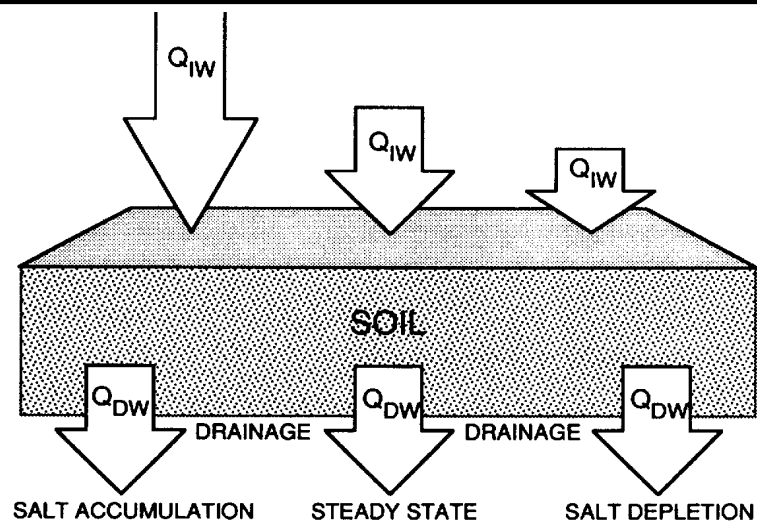
EC of saturated soil paste

- **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

- **Mg²⁺ and Ca²⁺ 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.)

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

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

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.**

$$\frac{NaX}{CEC} \cdot 100 = ESP$$

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

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%

15%	<p>pH > 9 Sodic Poor Dispersed</p>	<p>pH < 8.5 Saline-sodic Fair-good Flocculated</p>
	<p>pH < 8.5</p>	<p>pH < 8.5 Saline Good Flocculated</p>
	NORMAL	

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.**