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ASAC 1101 : FUNDAMENTALS OF SOIL SCIENCE (2+1)

Level : B.Sc (Ag), I semester

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SOIL SCIENCE AND AGRICULTURAL CHEMISTRY

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Topic

**pH, soil acidity and alkalinity, buffering,
Effect of pH on nutrient availability**

Concepts Covered:

- What is soil acidity?
- Natural and manmade causes of soil acidity
- Pools of soil acidity
- Ameliorating soil acidity

Soil acidity

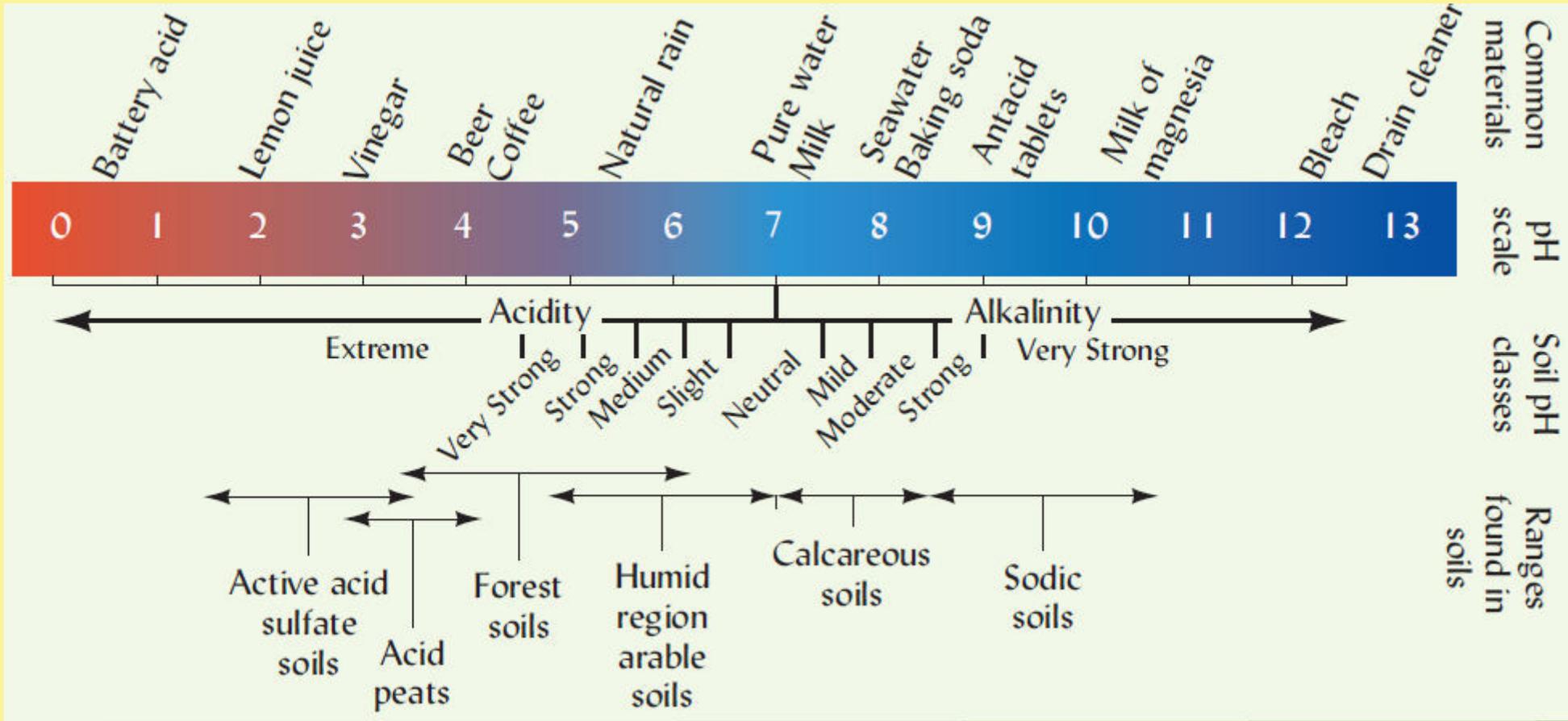
- ❑ Soil acidity is measured in pH units
- ❑ The smaller the pH, the more the acidity

$$pH = -\log[H^+]$$

[H⁺] : the concentration of H⁺ ions

- ❑ Every unit change in pH indicates a 10 fold change in acidity

Soil acidity



Sources of acidity

1. Carbonic and other organic acids

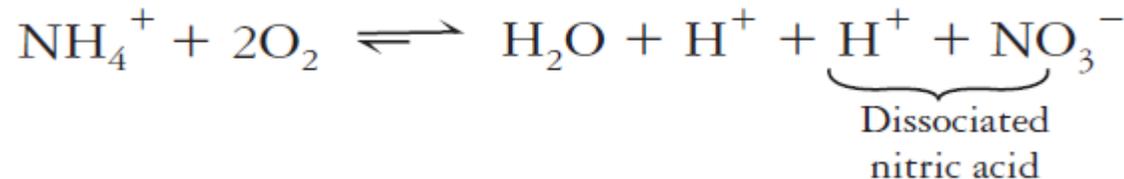
Source: CO₂ from respiration and organic matter decomposition



2. Accumulation of organic matter

3. Nitrification

Source: NH₄⁺ from fertilizers

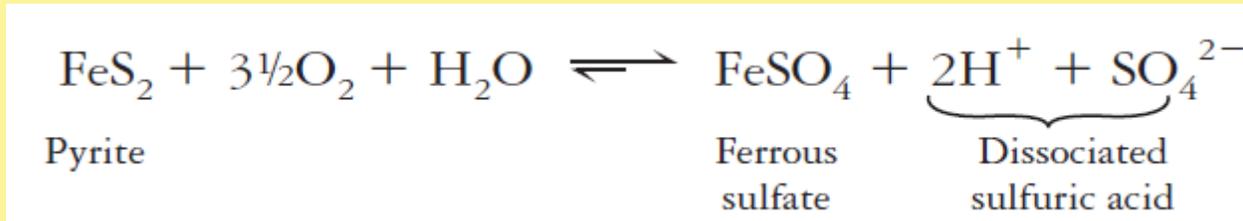


causes acidity

Sources of acidity

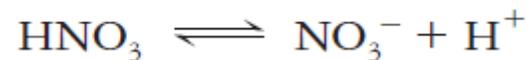
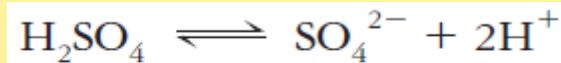
4. Sulphur oxidation

Source: pyrite parent material



5. Acid rain

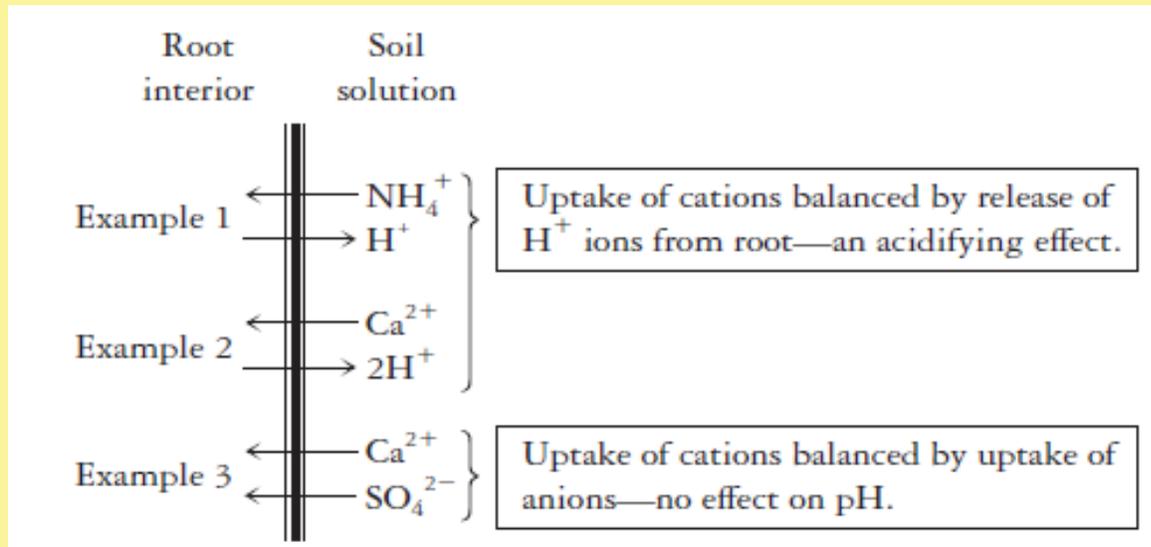
Source: Sulphur and nitrogen from forest fires, lightning etc.



Sources of acidity

6. Plant uptake of cations

When plant roots take up more cations, they tend to balance it by releasing a H^+ ion, lowering the soil pH



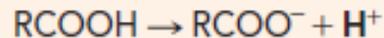
Balance between production and consumption of H⁺ ions

THE MAIN PROCESSES THAT PRODUCE OR CONSUME HYDROGEN IONS (H⁺) IN SOIL SYSTEMS

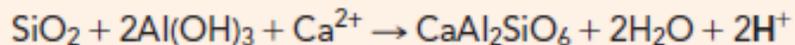
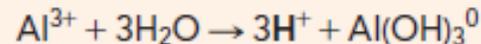
Production of H⁺ ions increases soil acidity, while consumption of H⁺ ions delays acidification and leads to alkalinity. The pH level of a soil reflects the long-term balance between these two types of processes.

Acidifying (H⁺ ion-producing) processes

Formation of carbonic acid from CO₂
Acid dissociation such as:



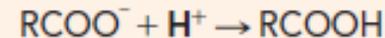
Oxidation of N, S, and Fe compounds
Atmospheric H₂SO₄ and HNO₃ deposition
Cation uptake by plants
Accumulation of acidic organic matter
Cation precipitation such as:



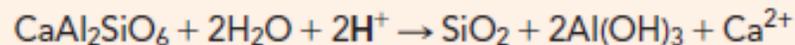
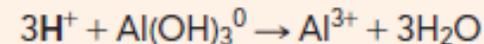
Deprotonation of pH-dependent charges

Alkalinizing (H⁺ ion-consuming) processes

Input of bicarbonates or carbonates
Anion protonation such as:

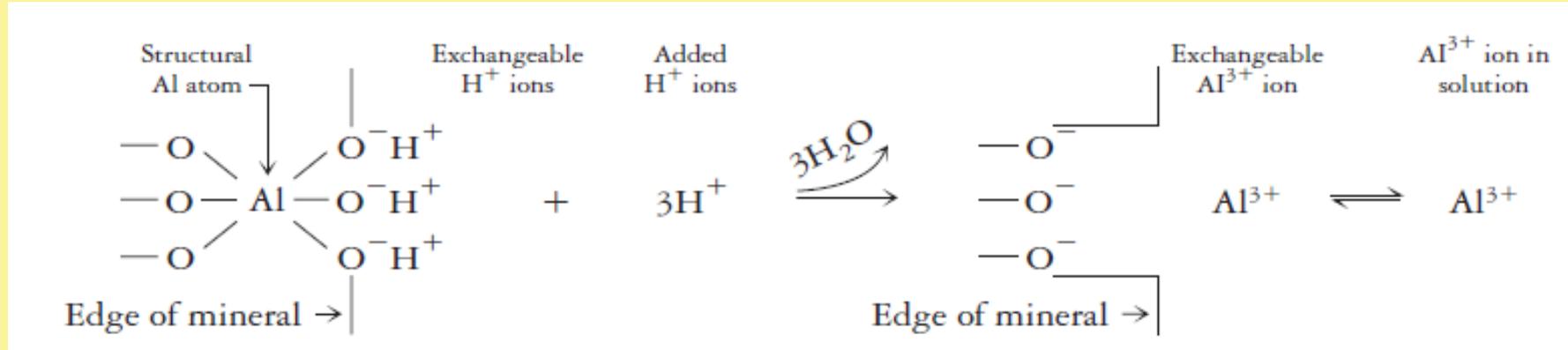


Reduction of N, S, and Fe compounds
Atmospheric Ca, Mg deposition
Anion uptake by plants
Specific (inner sphere) adsorption of anions (especially SO₄²⁻)
Cation weathering from minerals such as:

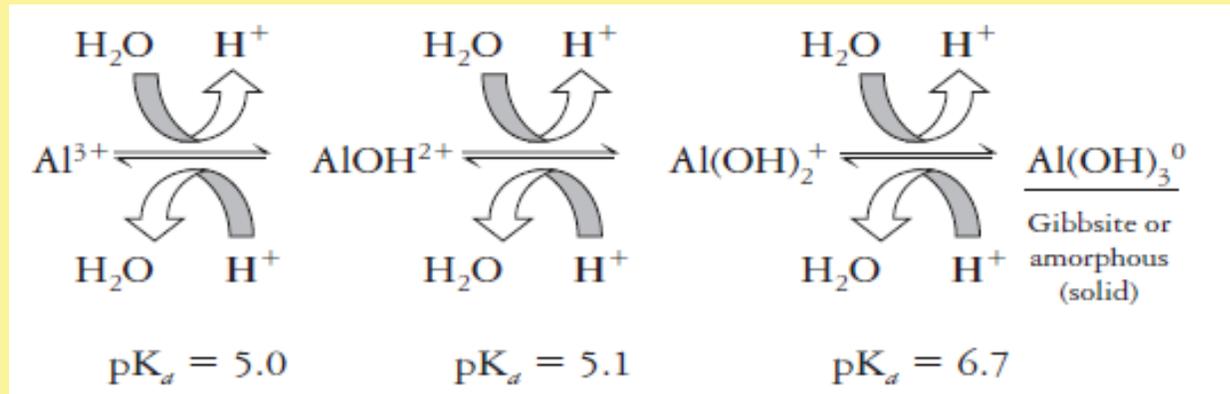


Protonation of pH-dependent charges

How aluminium causes soil acidity?

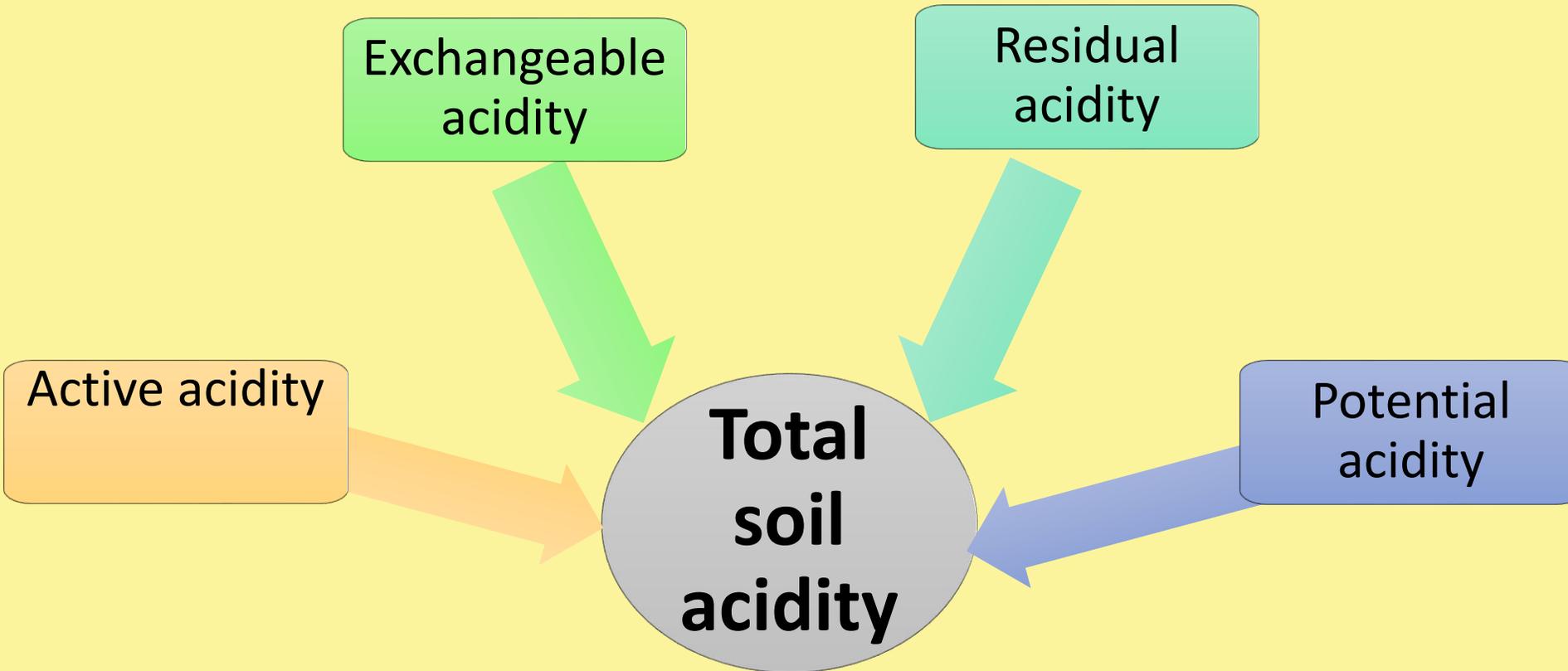


H⁺ releases aluminium from crystal structure and Al occupies exchangeable site of colloid



Each aluminium releases three H⁺ ions

Pools of soil acidity



Residual acidity > Exchangeable acidity > Active acidity

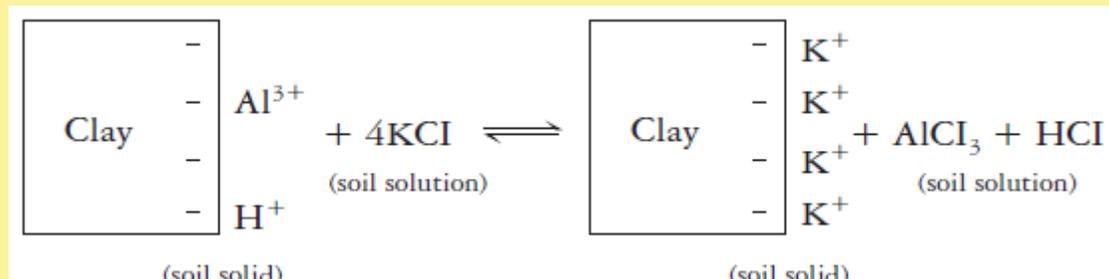
Pools of soil acidity

1. Active acidity

- ❑ This is the acidity usually measured using pH of soil solution
- ❑ Can be easily balanced

2. Exchangeable acidity

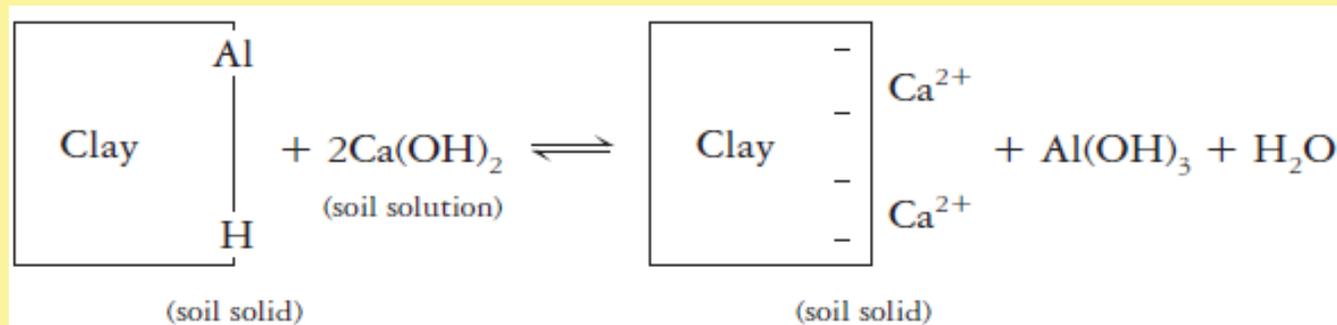
- ❑ Primarily caused by the Al^{3+} and H^+ ions in exchangeable sites in soil minerals (exchangeable cations)
- ❑ Can be measured by using unbuffered salts like KCl



Pools of soil acidity

3. Residual acidity

- Primarily caused by Al^{3+} and H^+ in non-exchangeable sites in soil colloid (bound cations)
- Released using liming materials



4. Potential acidity

- the maximal amount of acidity which a partly or totally reduced soil may contain after it has been completely oxidized

Cation saturation percentage

Saturation percentage: proportion of CEC occupied by a given ion

Base saturation: proportion of CEC occupied by non-acid cations
 Ca^{2+} , Mg^{2+} , K^{+} and Na^{+}

Acid saturation: proportion of CEC occupied by acid cations H^{+} and Al^{3+}

Example: CEC = 20 cmol/kg with 10 Ca^{2+} , 3 Mg^{2+} , 1 K^{+} , 1 Na^{+} , 1 H^{+} and 4 Al^{3+}

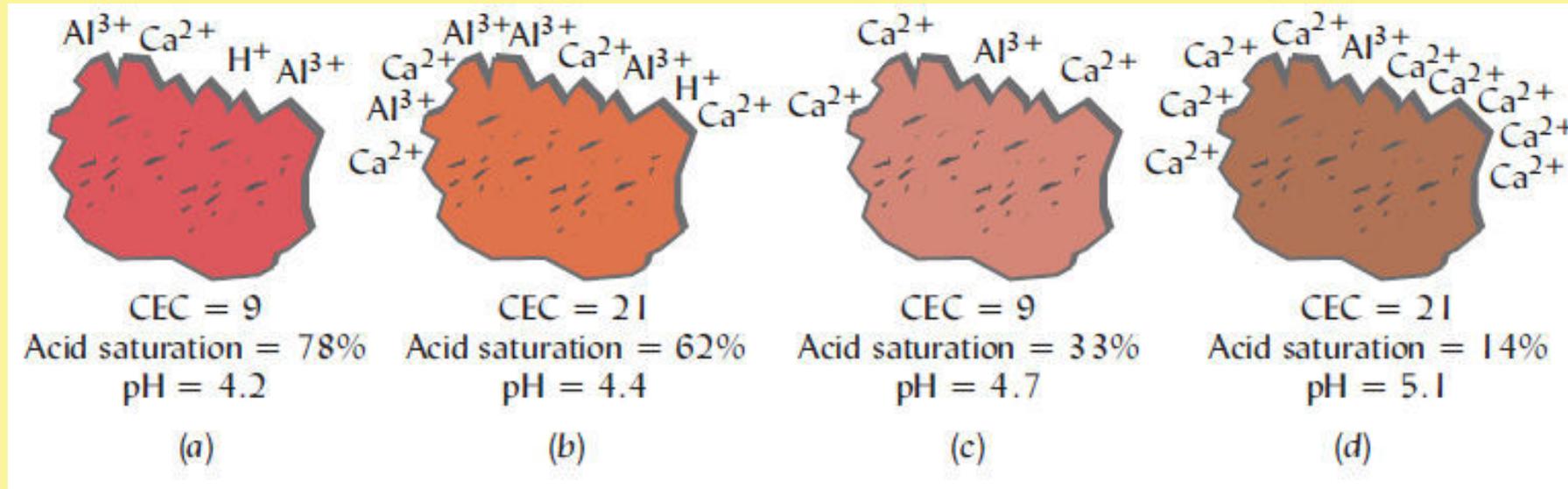
What is the magnesium saturation?

$$\frac{3}{20} * 100 = 15\%$$

What is the base saturation?

$$\frac{(10 + 3 + 1 + 1)}{20} * 100 = 75\%$$

Relation between CEC and type of cations



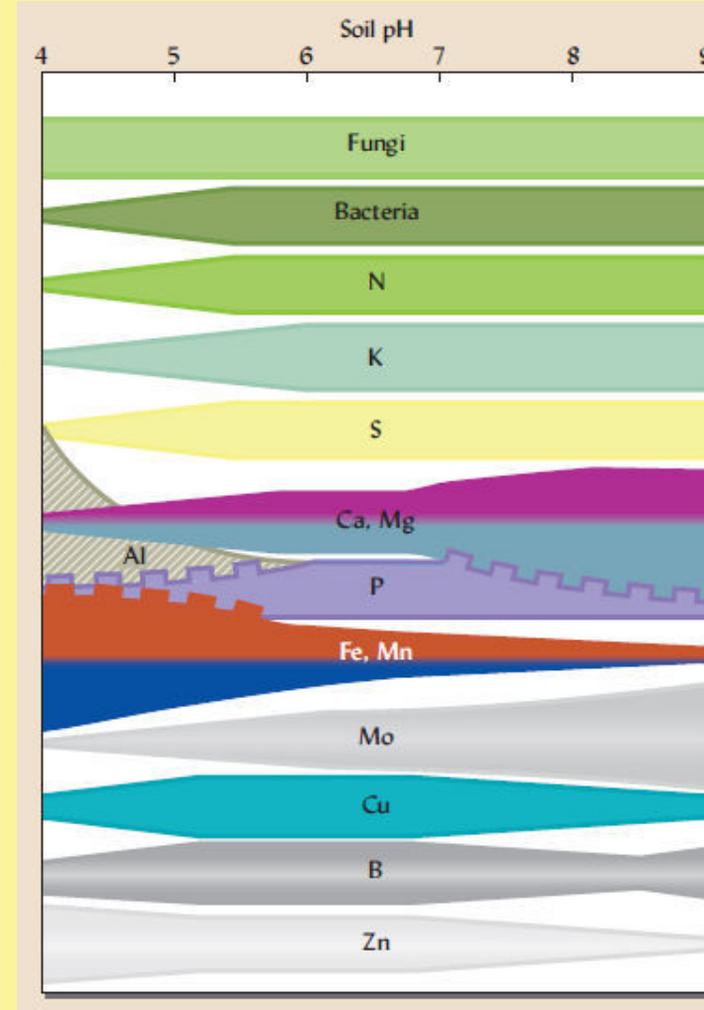
Even though soils (b) and (d) have same Cation Exchange Capacity, soil (d) has less acid saturation and therefore higher pH value than soil (b)

Why should we consider soil buffering capacity?

- Better buffered the soil, better it resists acidity from external factors
- Buffering capacity helps us determine the amount of lime to be applied to raise the pH
- Higher the CEC, more the buffering capacity of soil
- Compensating only active acidity will have little consequence while liming. Therefore, we should also consider other pools

Effects of acidity

- Aluminium toxicity
- Manganese, Iron and Hydrogen toxicity
- Nutrient availability to plants affected
- Affects microbial growth
- Optimal pH for plants affected



Amelioration of acidity

1. Application of liming materials

□ Example: CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, CaO , MgO , CaSiO_3 etc.



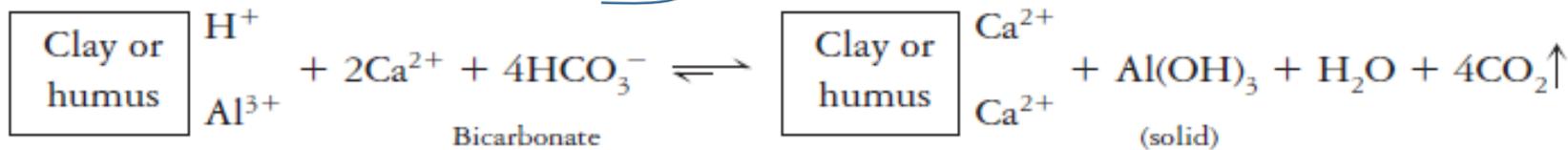
Dolomitic limestone

Bicarbonate

Bicarbonate

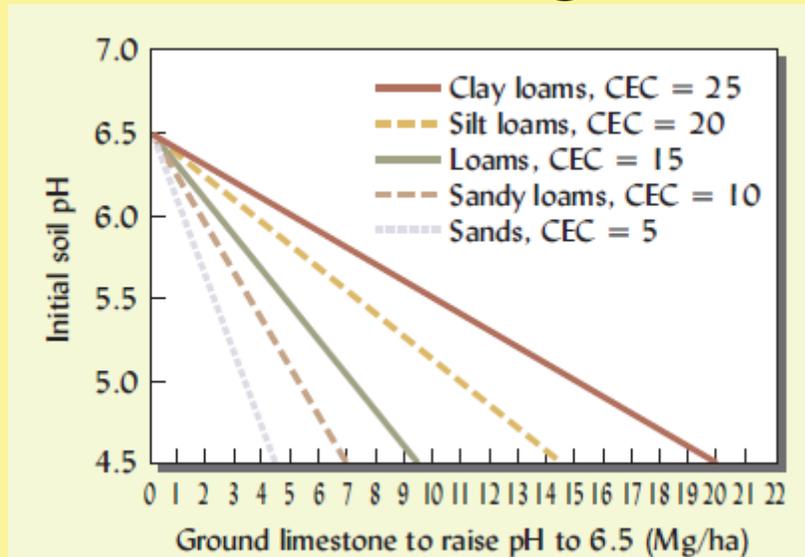
High CO_2 drives the reaction to right

Bicarbonate is very reactive in removing the Residual and exchangeable acidity



Amelioration of acidity

- Amount of lime used depends on pH target, depth of application, buffer capacity of soil, lime material used and fineness of liming material



Fine textured soils need more liming as their buffer capacity to resist change is more.
Split application of lime recommended

Amelioration of acidity

2. Using organic matter

- They bind with Al and reduce their mobility
- They complex Al into non-toxic forms

3. Growing adapted plants

- A very practical solution
- Crops native to acid soils can be cultivated
- Through genetic engineering, new resilient varieties are also developed

Reference:

- ❑ **The Nature and Properties of Soils by Nyle C. Brady and Ray R. Weil**

CONCEPTS COVERED

Concepts Covered:

- Causes of alkalinity and salinity
- Measurement of salinity and alkalinity
- Classification of saline soils
- Reclamation and management

Causes of salinity

- Saline soils are generally developed in arid and semi-arid condition.
- Evaporation should be more than precipitation.
- The pH of the soils are >8.5 .
- Saline soils are developed in crop fields not only due to the climate but also due to the use of saline irrigation water and poor drainage condition.
- Weathering of salt containing minerals.

Causes of high soil pH

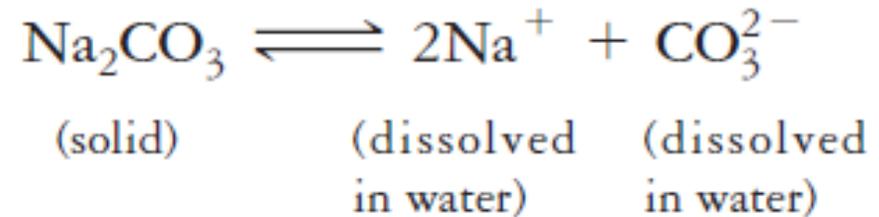
- Sources of alkalinity
- Influence of carbon dioxide and carbonates
- Role of the cations (Na^+ versus Ca^{2+})
- Influence of soluble salt level

Influence of Carbon Dioxide and Carbonates

- The amount of CO_2 in soil is always more than the atmosphere: respiration
- But it will reduce the pH of the soil driving the reaction to the left.
- The increase in pH stopped when Ca^{2+} increases in the soil solution as it increases the precipitation of CaCO_3 .
- The CaCO_3 precipitates at pH 7-8. So, in calcareous soil the pH never goes beyond 8.4.
- If Na_2CO_3 is present which is more soluble than CaCO_3 then pH can be increased up to 10.5.

Role of the Cations (Na⁺ Versus Ca²⁺)

- Na₂CO₃ is more water soluble than the CaCO₃.
- So, it produces more OH⁻ and CO₃⁻ and it increases the pH up to 10.



Influence of Soluble Salt Level

- The presence of the salts like CaSO_4 , NaCl , Na_2SO_4 , CaCl_2 etc. will reduce the alkalinity.
- The presence of common ions will drive the reaction to the left side.
- The *common ion effect* will reduce the dissolution of the CaCO_3 and Na_2CO_3 .

Development of salt-affected soils

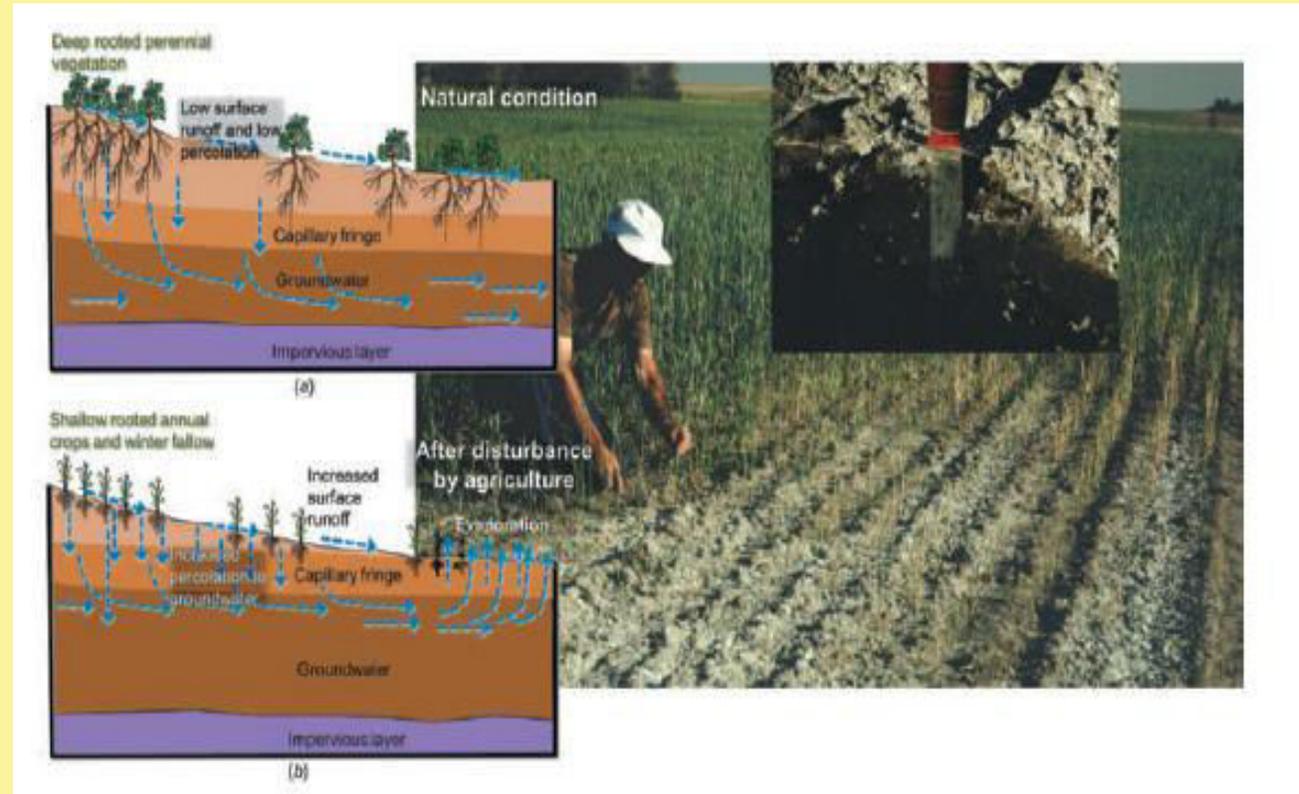
- Accumulation of salts in non-irrigated Soils
- Irrigation-Induced salinity and alkalinity



Accumulation of salts in Non-irrigated Soils

(a) Under deep-rooted perennial vegetation, transpiration is high and the water table is kept low.

(b) In case of agricultural crops, the length of the roots are small and it causes groundwater to rise by capillary flow to the surface.



Irrigation-induced salinity and alkalinity



- The irrigated water may contain huge or very less amount of salts.
- If, the field has not adequate drainage system, continuous evaporation accelerate the chance of salt accumulation.
- Salts tend to accumulate at the highest part of the soil surface from which part evaporation loss is the highest.

Measuring Salinity

DIFFERENT MEASUREMENTS FOR ESTIMATING SOIL SALINITY

The methods are well correlated, so each can be converted to any other. The EC_e is the most common standard for comparison.

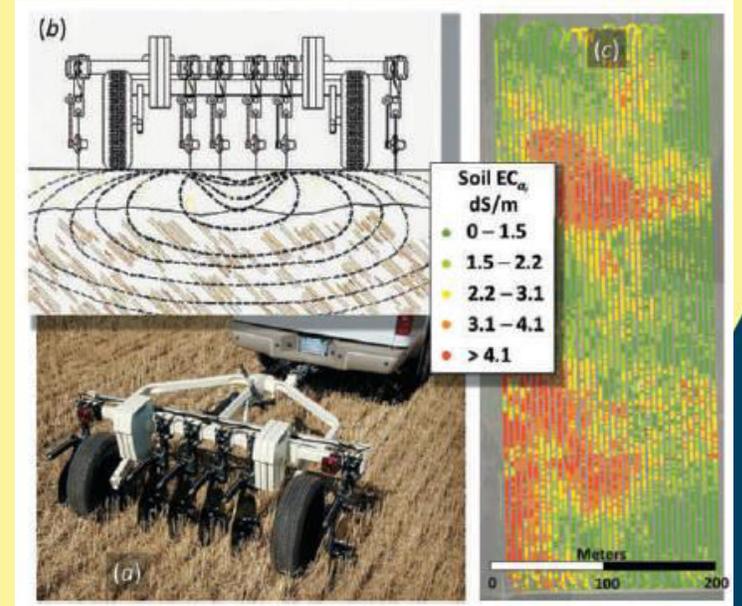
Measured on a soil sample

EC_e	Conductivity of the solution extracted from a water-saturated soil paste
EC_p	Conductivity of the water-saturated soil paste itself
EC_w	Conductivity of the solution extracted from a soil–water mixture (usually either 1:2 or 1:5)
EC_s	Conductivity of a 1:1, 1:2, or 1:5 soil–water mixture itself
TDS	Total dissolved solids in water or the solution extracted from a water-saturated soil paste ^a

Measured on bulk soil in place

EC_a	Apparent conductivity of bulk soil sensed by metal electrodes in soil
EC^*_a	Electromagnetic induction of an electric current using surface transmitter and receiving coils

^aNote that TDS (mg/L) can be converted to EC_w using these relationships between 0 and 5 dS/m: for Na salts, $TDS = 640 \times EC_w$ based on a 1:2 soil:water mixture; for Ca salts, $TDS = 800 \times EC_w$. The dilution effect of varying soil:water ratios must be taken into account when comparing data by the various EC_s and EC_w methods.



Measurement of sodium status

- Excess sodium destroys the physical properties of the soil which is called sodicity.
- It can be measured by different equations based on the relative amounts and flocculating ability of the various cations present.

1. Exchangeable Sodium Percentage

$$\text{ESP} = \frac{\text{Exchangeable sodium, cmol}_c/\text{kg}}{\text{Cation exchange capacity, cmol}_c/\text{kg}} \times 100$$

- ESP measures the degree to which the exchange complex is saturated with sodium.
- ESP levels greater than 15 are associated with severely deteriorated soil physical properties and pH values of 8.5 and above.

Measurement of sodium status

2. Sodium Adsorption Ratio (SAR) is the second, more easily measured property that is becoming even more widely used than ESP. The SAR gives information on the comparative concentrations of Na^+ , Ca^{2+} , and Mg^{2+} in soil solutions.

$$\text{SAR} = \frac{[\text{Na}^+]}{(0.5[\text{Ca}^{2+}] + 0.5[\text{Mg}^{2+}])^{1/2}}$$

where $[\text{Na}^+]$, $[\text{Ca}^{2+}]$, and $[\text{Mg}^{2+}]$ are the concentrations (in mmol of charge/l) of the sodium, calcium, and magnesium ions in the soil solution.

- An SAR value of 13 for the solution extracted from a saturated soil paste is approximately equivalent to an ESP value of 15.
- It is used for characterizing the irrigation water.

Classes of salt-affected Soils

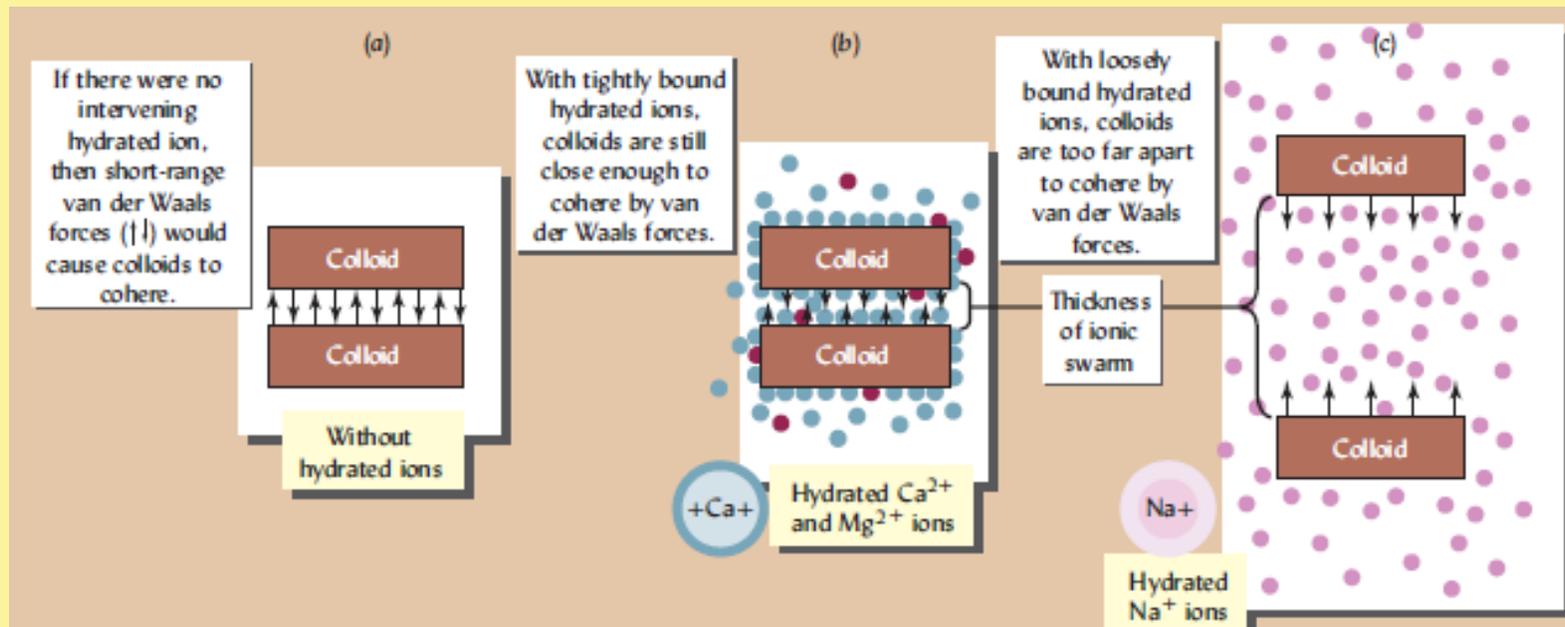
Properties	Saline soil (White alkali)	Saline-sodic soil	Sodic soil (Black alkali)
Structure	Very good	Good	Structure less
pH	Around 8.5.	$8.5 < \text{pH} < 10$	> 10
EC	> 4 dS/m	> 4 dS/m	< 4 dS/m
ESP	< 15	> 15	> 15
SAR	< 13	> 13	> 13
Major ions	Mainly Ca^{2+} and Mg^{2+} and SO_4^{2-} , Cl^-	Salts of Ca^{2+} and Mg^{2+} with Na^+	Mainly Na^+ and CO_3^{2-} - HCO_3^-

Sodic Soils

- Sodic soils are, perhaps, the most troublesome of the salt-affected soils.
- $EC < 4$ dS/m but $SAR > 13$ and $ESP > 15$.
- The pH of the sodic soil exceed 8.5, rising to 10 or higher in some cases.
- The high pH is caused due to the presence of sodium carbonate which is highly soluble.
- So, the soil contains a high amount of CO_3^{2-} and HCO_3^- ions in the solution.
- At this high pH cause FA and HA of organic matter to dissolve. When the water evaporates, can give soil surface a black colour. These soils are called black alkali.

Physical degradation of soil by sodic chemical condition

- Slaking, Swelling, and Dispersion
- Two Causes of Soil Dispersion-High Sodium and Low Salt Concentration



- The plant growth is hampered due to the toxicity of Na^+ , OH^- and HCO_3^- .
- These soils have columnar structure.
- Extremely poor soil physical conditions, slow permeability to water and air and clay dispersion reduces the crop productivity.



Columnar structure of Sodic soil

Leaching Requirement (LR)

The amount of water needed to remove the excess salts from saline soils, called the LR.

The salt balance equation is –

S_{iw} - salt from irri water

S_p - atms deposition

S_f - fertilizers

S_m - soil minerals

S_{dw} - drainage water

S_c - Crop removal

S_{ppt} - chemical precipitation of sulphate and carbonates

$$S_{iw} + S_p + S_f + S_m = S_{dw} + S_c + S_{ppt}$$

Salt inputs

Salt outputs

- The main concern is to balance the salt coming in with the irrigation water and that leaving with the drainage water:

$$S_{iw} = S_{dw}$$

The amount of salt is calculated as the product of the volume of the water in cm and the amount of salts = $D * EC$

So, the equation will be-

$$D_{iw} * EC_{iw} = D_{dw} * EC_{dw}$$

$$\rightarrow EC_{iw} / EC_{dw} = D_{dw} / D_{iw}$$

$$\rightarrow EC_{iw} / EC_{dw} = \text{Leaching requirement}$$

Example:

Consider the situation where the irrigation water has an EC_{iw} of 2.5 dS/m and a moderately tolerant crop (e.g., broccoli) is to be grown. For a moderately tolerant crop, we can use 8 dS/m as the acceptable EC_{dw} to produce 90% of the maximum yield.

$$LR = \frac{2.5 \text{ dS/m}}{8 \text{ dS/m}} = 0.31$$

0.31 is multiplied by the amount of water ($0.31 * 12\text{cm water} = 3.7 \text{ cm}$). 3.7cm water is the minimum amount of water needed to maintain the root zone salinity at the acceptable level.

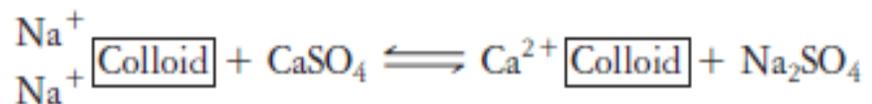
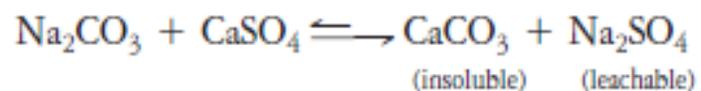
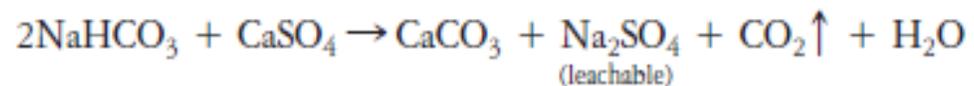
Management of soil salinity

- Irrigation water quality
- Growing salt tolerate crops

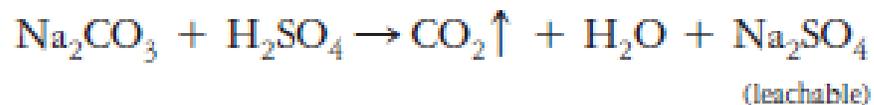
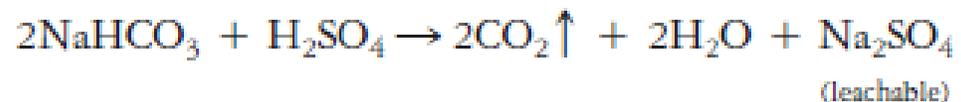
Reclamation of saline–sodic and sodic soils

- The Na^+ ion is replaced by other cations (Ca^{2+} mainly).
- pH of the soil is reduced by adding acid forming substances.
- Gypsum is generally used to reclaim sodic soil where exchange complex does not have Ca^{2+} ions.
- Otherwise any acid forming substances can be used for reclamation where Ca^{2+} ions are present in the exchange complex.

Gypsum



Sulfur and Sulfuric Acid



Problem

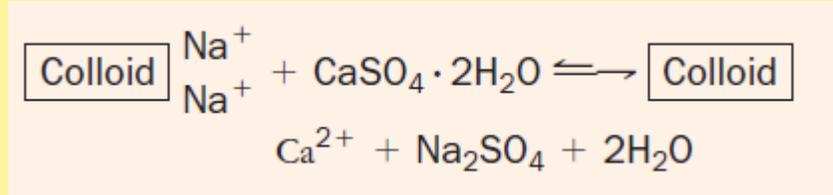
- How much gypsum is needed to reclaim a sodic soil with an ESP of 25% and a cation exchange capacity of 18 cmolc/kg? Assume that you want to reduce the ESP of the upper 30 cm of soil to about 5% so that a crop like alfalfa could be grown.

- Solution

First, determine the amount of Na⁺ ions to be replaced by multiplying the CEC (18) by the change in Na⁺ saturation desired (25 - 5 = 20%).

$$18 \text{ cmolc /kg} * 0.20 = 3.6 \text{ cmolc /kg}$$

From the reaction that occurs when the gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is applied,



3.6 cmolc of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will be needed to replace 3.6 cmolc of Na^+ .

- Second, calculate the weight in grams of gypsum needed to provide the 3.6 cmolc/kg soil. This can be done by first dividing the molecular weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (172) by 2 (since Ca^{2+} has two charges and Na^+ only one) and then by 100 since we are dealing with centimole rather than mole.**

$$172/2 = 86 \text{ g CaSO}_4, 2\text{H}_2\text{O/molc}$$

and

$$86/100 = 0.86 \text{ g CaSO}_4, 2\text{H}_2\text{O/cmolec required to replace 1 cmolec Na}^+$$

The 3.6 cmol Na⁺/kg would require 3.6 cmol /kg * 0.86/cmolec = 3.1 g CaSO₄, 2H₂O/kg of soil.

- Last, to express this in terms of the amount of gypsum needed to treat 1 ha of soil to a depth of 30 cm, multiply by 4*10⁶, which is twice the weight in kg of a 15-cm-deep hectare–furrow slice

$$3.1 \text{ g /kg} * 4 * 10^6 \text{ kg/ha} = \underline{12,400,000 \text{ g gypsum/ha}}$$