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Sodic Soil and Their Management

Dr. Arunabha Pal



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Outline

- **Introduction to sodic soil**
- **Causes of poor productivity of sodic soil**
- **Evaluation/Appraisal of sodic problem**
- **Management strategies for combating sodicity problem**



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Sodic Soil

In sodic soil a crux of the problem is the presence of high amount of exchangeable Na and as a result the physical property of soil is poor. Soil is in disperse condition and drainage is very poor

Most important distinguishing characteristics of sodic soils

- (i) High Exchangeable Na content- associated with high pH**
- (ii) Physical properties are very poor-eg. Structure, Aeration , permeability are very poor and tillage operation is very difficult**

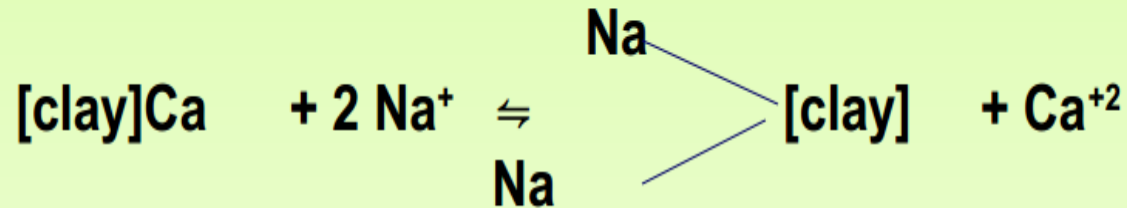


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Causes of Sodic Soil Development:

- i) **Salt accumulation** is the first stage of the formation of sodic soils
- ii) It is the result of **exchange of cations** in soil soln (especially Na^+) with those present on the exchange complex of the soil



- iii) The condition which result in **increase of SAR** of soil soln leads to the formation of sodic soil
- iv) It occurs in the **low lying area with insufficient natural drainage** where the products of weathering accumulate during rainy season.



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Causes of poor productivity of sodic soil

(i) High content of Na^+ ions (exchangeable) coupled with high pH have a toxic action on roots and roots are damaged. Under extreme cases the roots and the soil organic matter present in the soil get dissolved.

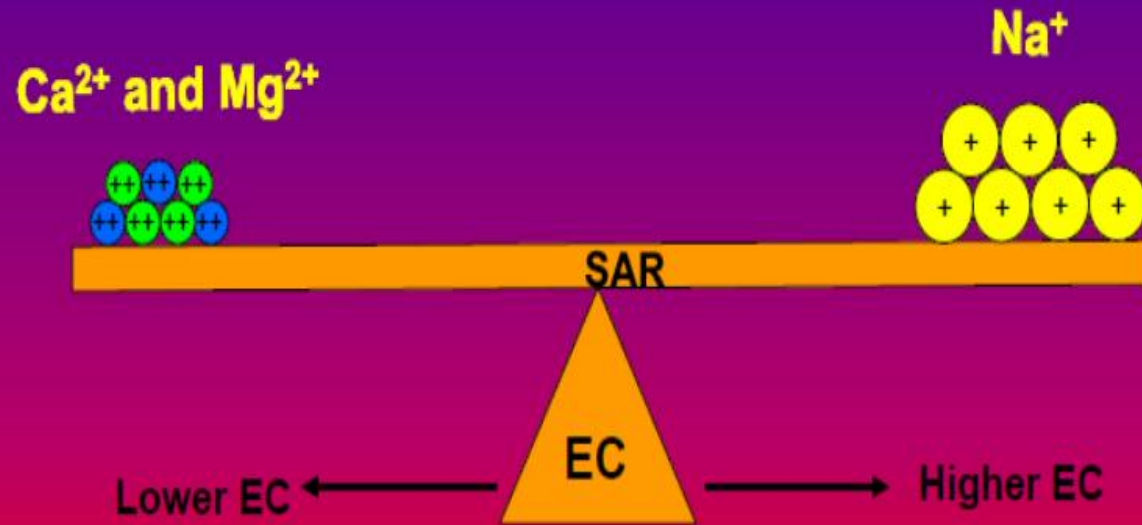
(ii) Poor aeration is another important cause of poor productivity of soil. Roots can't get sufficient oxygen from soil soil atmosphere. CO_2 of soil atm is very high and O_2 is low. So roots can not respire and resulted in poor productivity

(iii) Deflocculation and swelling of clay due to high exchangeable Na. This cause the tillage operation very difficult so causes the poor productivity



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Aggregate stability (dispersion and flocculation) depends on the balance (SAR) between (Ca^{2+} and Mg^{2+}) and Na^+ as well as the amount of soluble salts (EC) in the soil.



Tip the scale this way and you will flocculate the soil

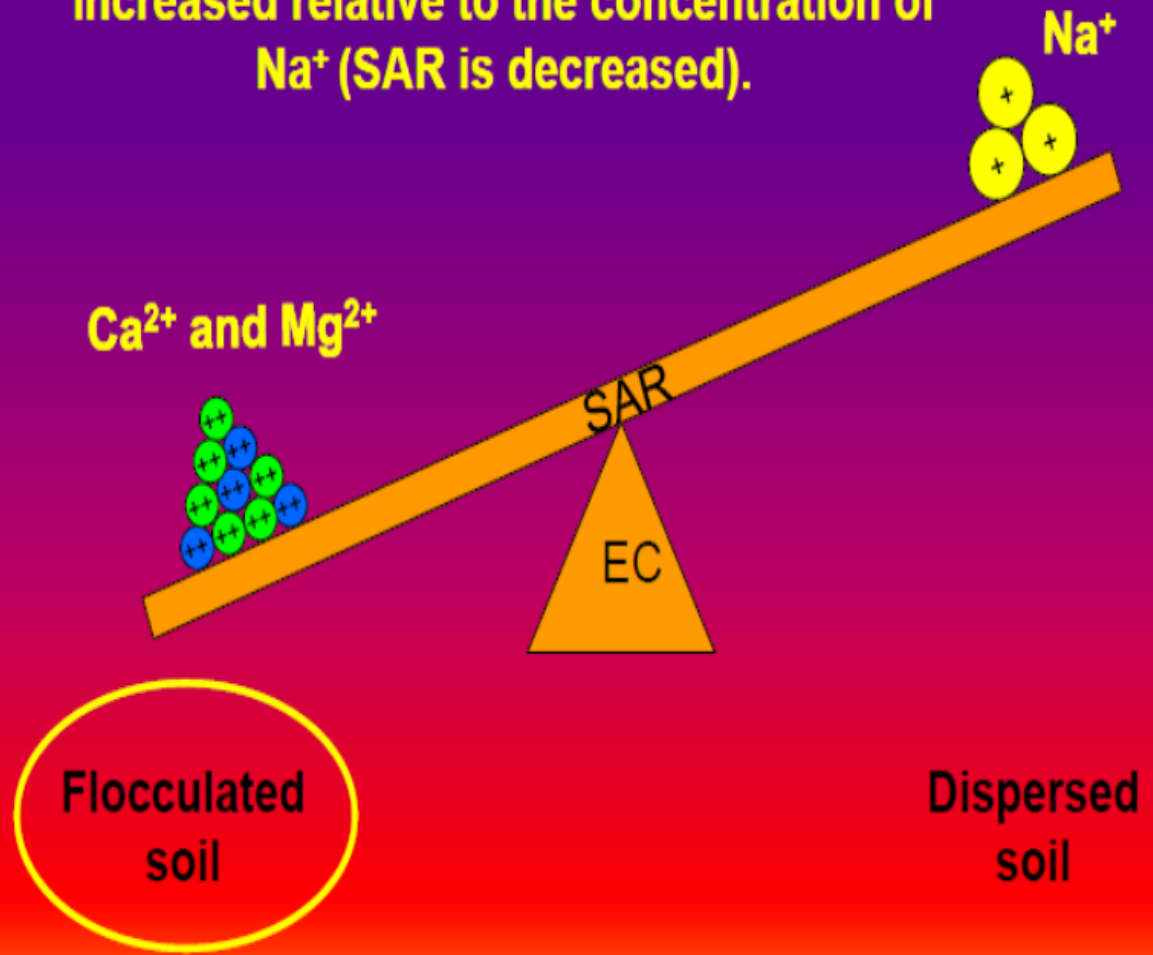
Dispersed soil



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Soil particles will flocculate if concentrations of $(Ca^{2+} + Mg^{2+})$ are increased relative to the concentration of Na^+ (SAR is decreased).



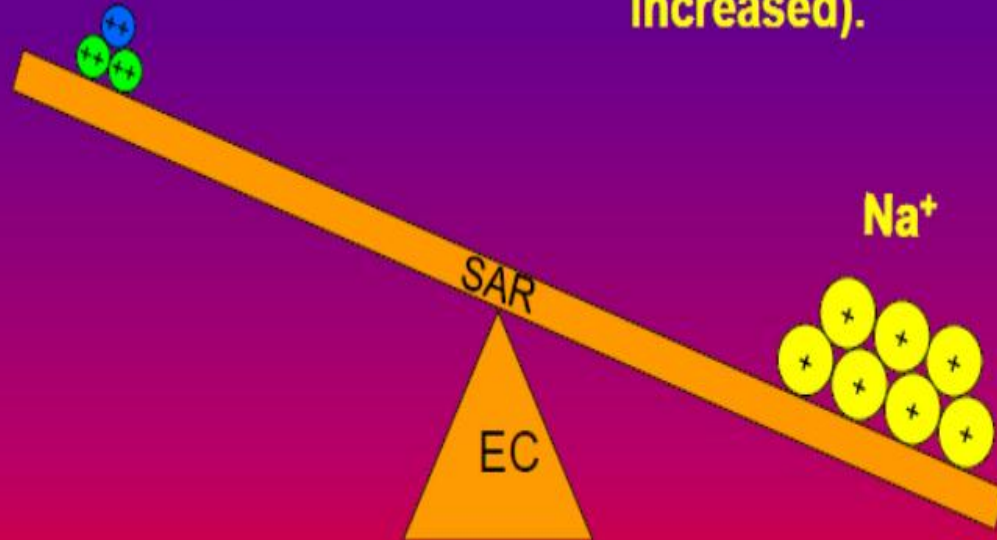


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Soil particles will disperse if concentrations of ($\text{Ca}^{2+} + \text{Mg}^{2+}$) are decreased relative to the concentration of Na^+ (SAR is increased).

Ca^{2+} and Mg^{2+}



Na^+

**Flocculated
soil**

**Dispersed
soil**

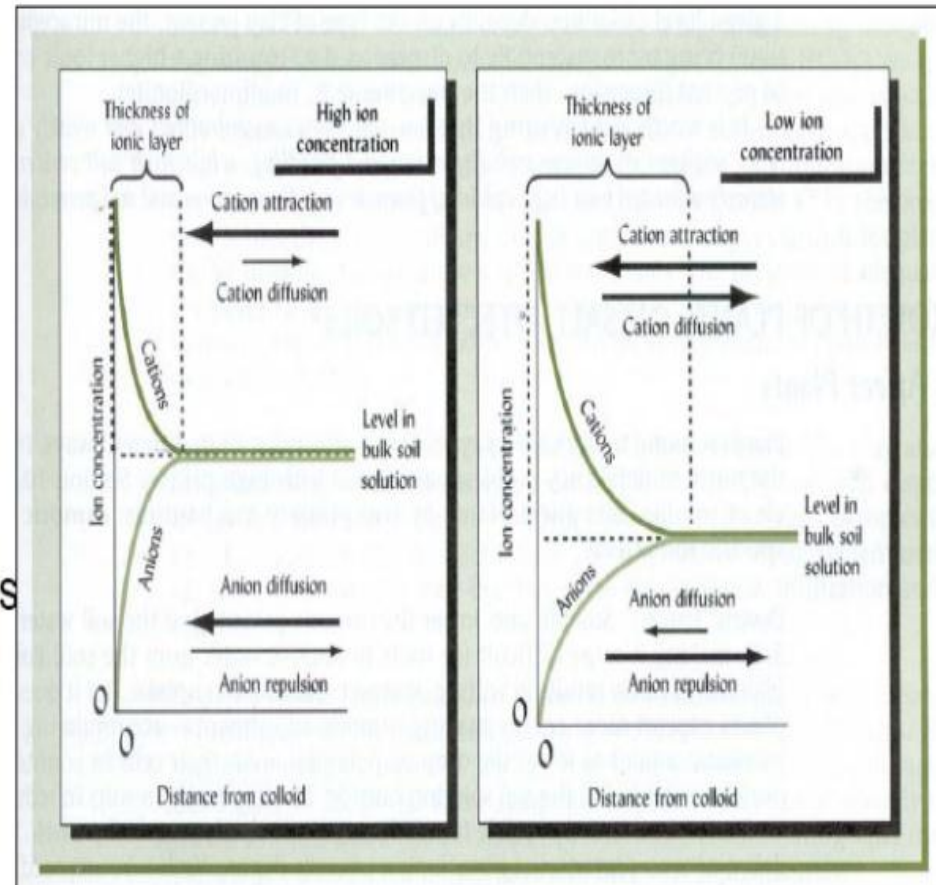


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Soil dispersion (high Na, low salt)

High salts:
cations
stay closer
and anions
come closer
to clay;
ionic swarm is
compressed;
floculation

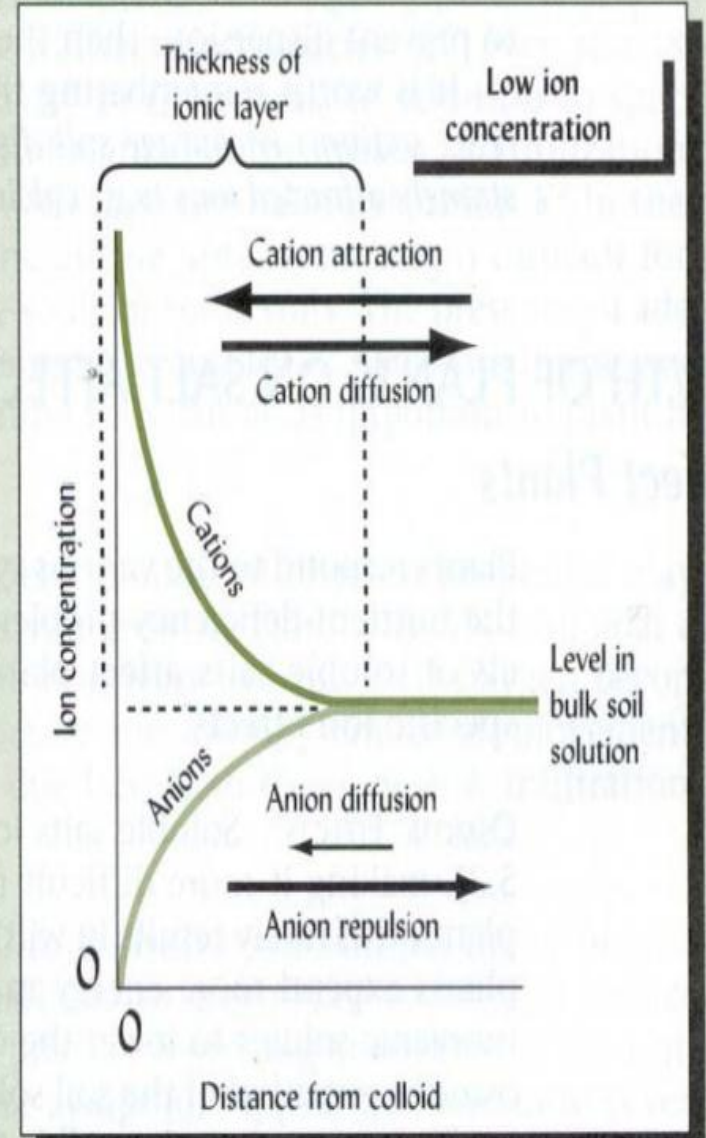
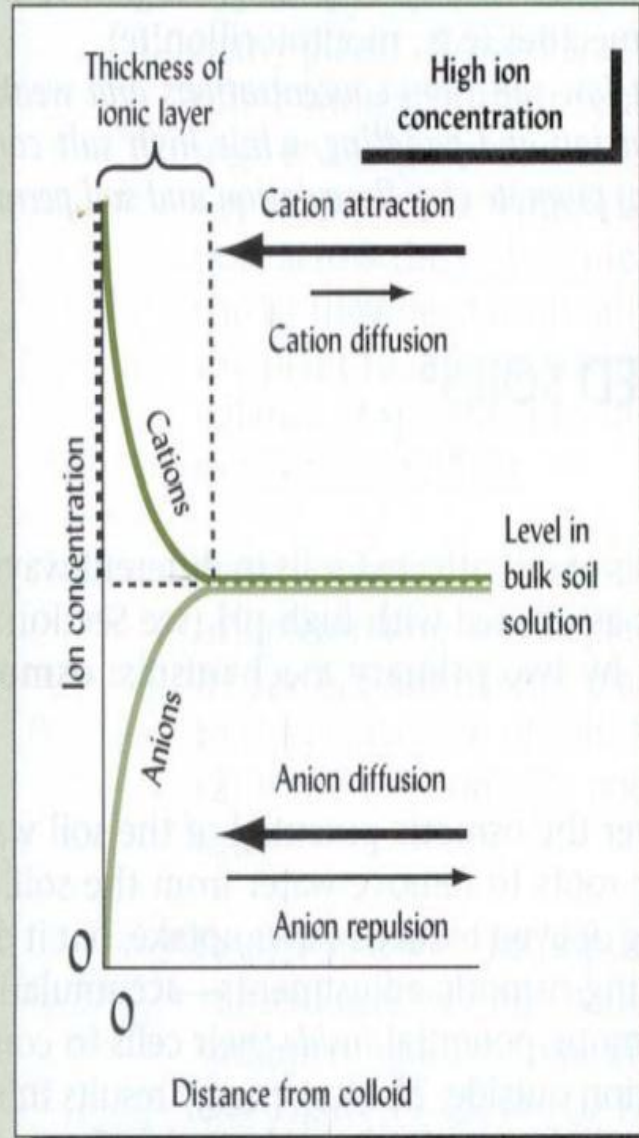


Low salts:
cations
diffuse away
from clay,
anions move
from clay;
ionic swarm
is expanded;
dispersion



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Flocculation - Dispersion...

1. Affect of Cation Type

Cations with a relatively small hydrated radius (Ca^{++} , Mg^{++}) form thin double layer, soil particles get close enough for short range attractive forces to cause flocculation.

Cations with a relatively large hydrated radius (Na^{+}) form thick double layer, soil particles cannot approach each other causing dispersion (recall... Calgon ~ PSA)

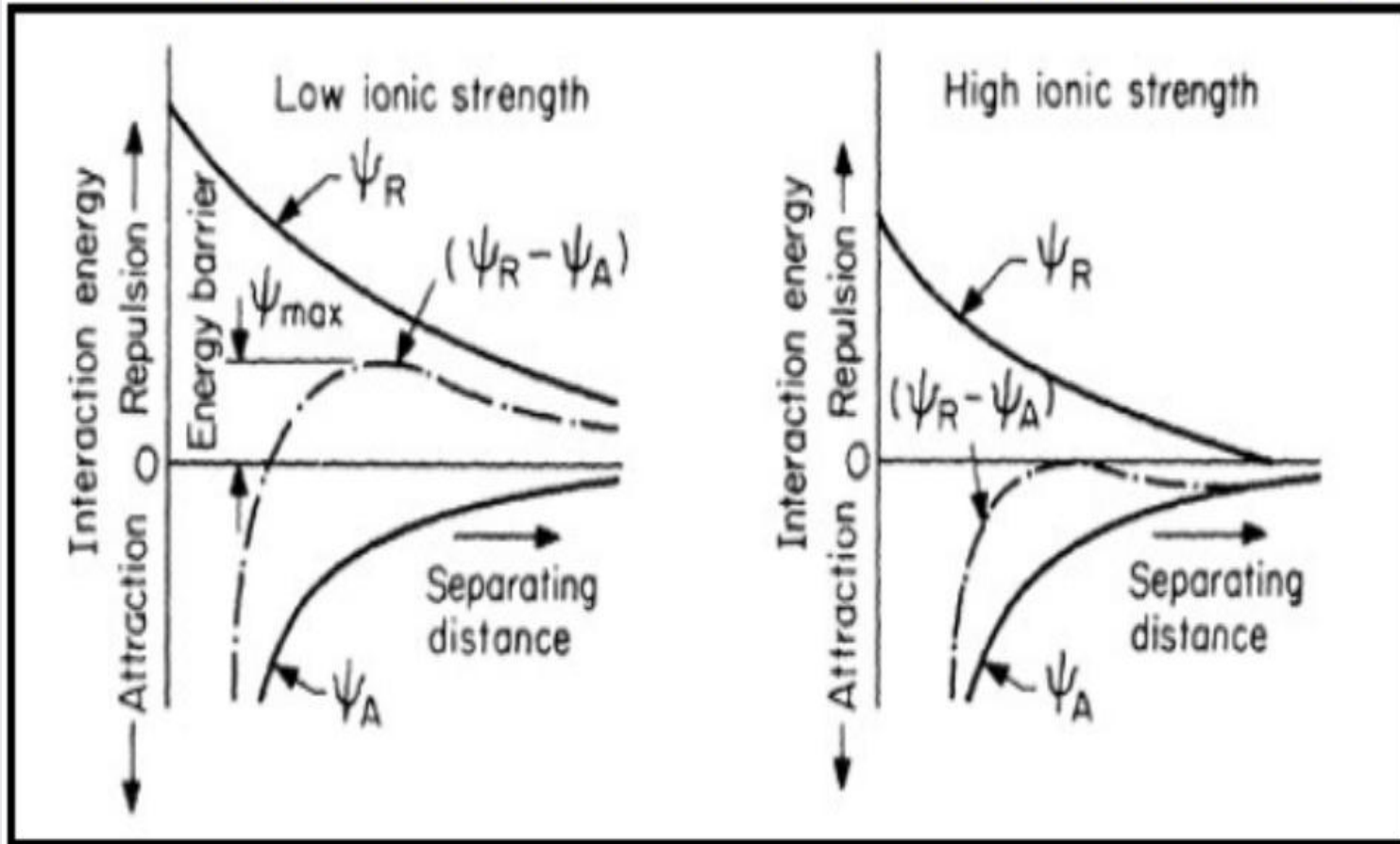


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Dispersed colloids

Flocculated colloids



Schematic diagrams showing the electrostatic repulsive potential ψ_R , the van der Waals attractive potential ψ_A , and the total potential $\psi_R - \psi_A$. The left diagram corresponds to dispersed colloids; the right diagram corresponds to flocculated colloids.



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Flocculation - Dispersion...

2. Affect of Electrolyte concentration:

High electrolyte concentration forms thin double layer therefore causes flocculation

Low electrolyte concentration forms thick double layer therefore causes dispersion

The **DLVO** (**Derjaguin** and **Landau**, 1941, and **Ver Wey** and **Overbeek**, 1948) theory of colloid stability states that dispersion or flocculation depends on the **net effect of van der Waals forces of attraction and electrical double layer forces of repulsion**. The collision efficiency, the probability of agglomeration when two particles collide, is also important to stability of the colloidal system.



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Dispersed Clay Particles



Before rehabilitating the arboretum soils, the clay was collapsed, hard, and sealed to percolation of water.



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Flocculated Clay Particles



***Arboretum soils today, showing the clay now aggregated and not sealed.
It's Humic Acids chelating the flocculating cations that do this!***



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$$\text{E.S.P} = (\text{Exch. Na}^+ \text{ content} / \text{CEC of the soil}) \times 100$$

Both CEC and Exch Na⁺ expressed as **meq/100g soil**

Factors on which the adverse effect of high exchangeable Na⁺ content depends:

- (i) Texture:** Physical properties of fine textured soils are more adversely affected than the coarse textured soil both having same ESP value.
- (ii) Type of Clay:** Abundance of expanding lattice type clay minerals such as montmorillonite, vermiculite etc., affects the physical properties of sodic soils more adversely than the non-expanding type of clay minerals such as Kaolinite, illite etc.
- (iii) Organic matter content of the soil:**
The higher the organic matter content the lesser is the unfavourable effect of high Exch Na⁺.
- (iv) K status and soluble silicate content:** The higher these constituents, the lesser is the adverse affect due to high exchangeable Na

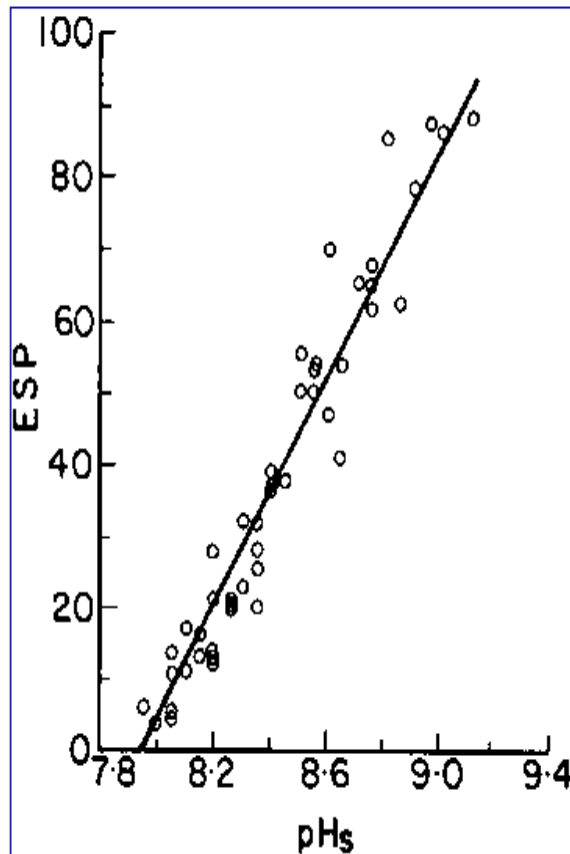


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Evaluation or appraisal of the sodic problem:

(i) Measurement of pH of the soil: There are very good correlation exists between pH and ESP. So from the pH of the soil we can determine or have an idea about the magnitude of ESP. So, higher the pH value, higher is the ESP value.



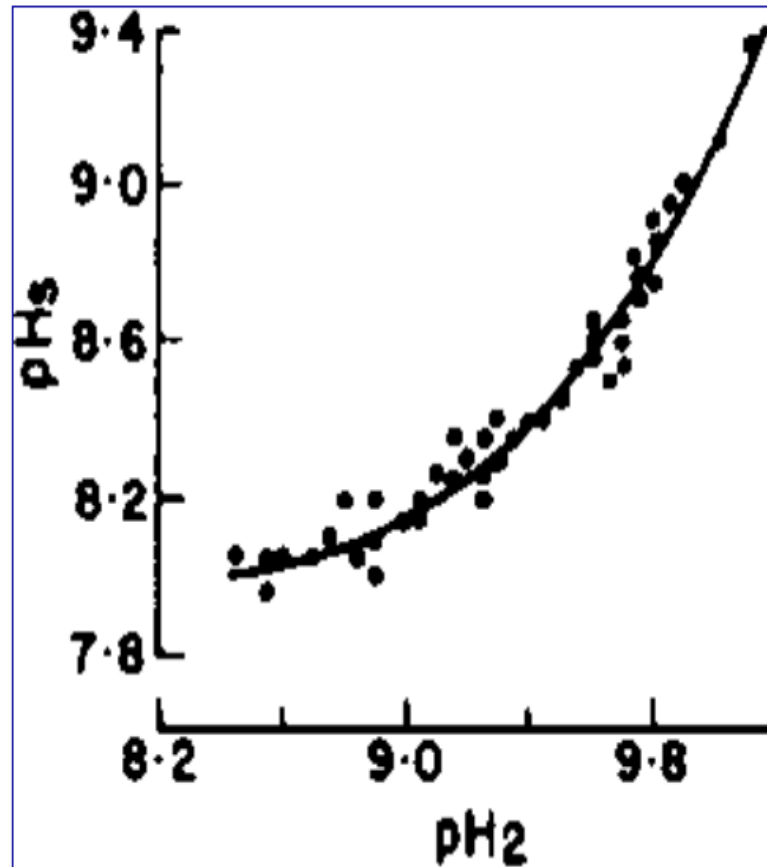
Relationship between the pH of saturated soil paste, and exchangeable sodium percentage (ESP) (Abrol et al., 1980)



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(ii) Measurement of change in pH between saturated soil paste and soil water suspension



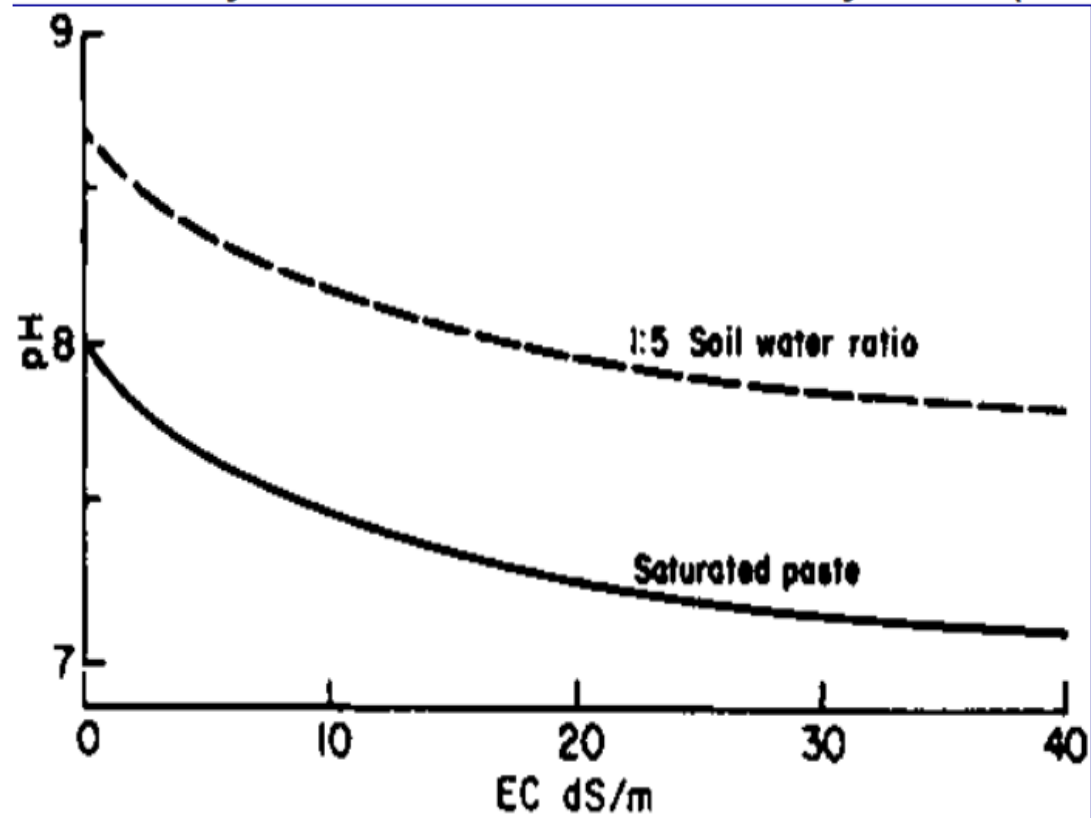
Relationship between pH of saturation paste, pH_s and pH of 1:2 soil-water suspension, pH_2 for soil of varying ESP



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Soil pH as affected by soil-water ratio and the salinity status (Dregne, 1976)



The **difference between pH of the saturated paste and 1:2 or 1:5 soil-water suspension tends to be greater in sodic** than in non-sodic or saline soils. This observation has led to the suggestion that a **difference of about 1 pH unit between the two readings indicates that the soil contains more than 15 % exch. Na^{\pm}** . This leads to the conclusion that when properly measured, pH can be used as a criterion for distinguishing sodic from normal and saline soils.



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(3) Determination of ESP

$$\text{ESP} = \frac{\text{Exchangeable Na (me/100 g soil)}}{\text{Cation exchange capacity (me/100 g soil)}} \times 100$$

For determination of ESP we have to measure exchangeable Na and CEC of the soil. The measurement of **CEC of the sodic soil is difficult** and also sometime erroneous because of the following reasons:

- (a) **NH₄⁺ fixation**
- (b) **Presence of water soluble salts**
- (c) **Poor leaching**

Incomplete removal of index salt solution during the **washing step of CEC determinations can lead to high CEC values and therefore low ESP** estimates. Similarly, **hydrolysis of exchangeable cations** during the removal of the index salt solution, **fixing of ammonium ions** from the index or replacement solution by the soil minerals and the **dissolution of calcium carbonate or gypsum in the index or replacing solutions** can all lead to low values of cation exchange capacity and therefore to high ESP estimates.



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To overcome some of these difficulties several workers prefer to obtain an estimate of the exchangeable sodium percentage from an analysis of the saturated soil extract.

Workers at the **US Salinity Laboratory** (Richards 1954) proposed that the sodium adsorption ratio (SAR) of the soil solution adequately defines the soil sodicity problem and is quantitatively related to the exchangeable sodium percentage of the soils. Sodium adsorption ratio, SAR, is defined by the equation:

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



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Exchangeable sodium percentage is related to the relative ratio of Na to $\text{Ca}^{1/2}$ in the solution phase, which is referred to as the SAR (see Chapter 4). An empirical relationship between SAR and ESP, representing soils of the arid west, was developed by the U.S. Salinity Laboratory Staff (1954):

$$\text{ESP} = \frac{100(-0.0126 + 0.01475 \text{ SAR})}{1 + (-0.0126 + 0.01475 \text{ SAR})}$$

$$\text{ESP} = 100 \frac{[\text{Na}_{\text{ex}}]}{[\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}]} = K_G \frac{\text{Na}^+}{[\text{Ca}^{++} + \text{Mg}^{++}]^{1/2}} = K_G \text{ SAR}$$

2



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4. Measurement of Gypsum requirement (GR)

A small quantity of sample soil is added to a relatively large vol. of std., nearly saturated gypsum soln., a loss in Ca from the soln., not compensated for by gain in Mg is defined as the GR of the soil.

The amount of gypsum required to be added to a sodic soil to lower the ESP to a desired value.

$$\text{GR} = (\text{ESP}_i - \text{ESP}_f) \times \text{CEC} / 100 \quad \text{.....(meq/100g)}$$



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Reclamation and Management

Basically, reclamation or improvement of sodic soils requires the removal of part or most of the **exchangeable sodium and its replacement by the more favourable calcium ions in the root zone**. This can be accomplished in many ways, the best dictated by **local conditions, available resources and the kind of crops to be grown** on the reclaimed soils.

Kind of amendments

Chemical amendments for sodic soil reclamation can be broadly grouped into **three (3) categories**:

- (i) **Water Soluble calcium salts**, e.g. **Gypsum**, **Calcium chloride**
- (ii) **Acids or acid forming substances**, e.g. **Pyrites**, **Sulphuric acid**, **iron sulphate**, **aluminium sulphate**, **lime-sulphur**, **sulphur**,, etc.
- (iii) **Calcium salts of low solubility**, e.g. **ground limestone** , **by product lime of sugar factory**



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Categorisation of Alkali soils for the purpose of reclamation

- (i) Alkaline soils which contain alkaline earth carbonates (CaCO₃, MgCO₃), and have high pH
- (ii) Alkali soils which **do not contain alkaline earth carbonate** and **not have high pH** (near pH ... 7.5)
- (iii) Alkali soils which do not have alkaline earth carbonate but have high pH



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Alkali soil

➤ High alkaline earth carbonate but have high pH

➤ Do Not have alkaline earth carbonate and do not have high pH

➤ Low alkaline earth carbonate but have high pH

Amendments

Acids or acid formers :
Pyrites, Sulphuric acid, iron sulphate, Aluminium sulphate, lime-sulphur, sulphur,

ground limestone ,
by product lime of
sugar factory

CaCl_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum)

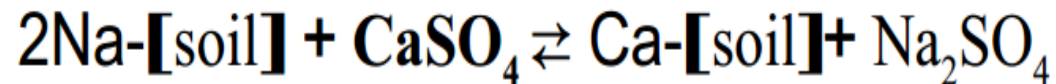
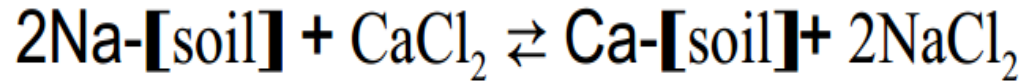


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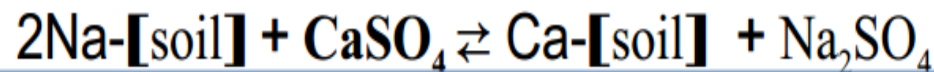
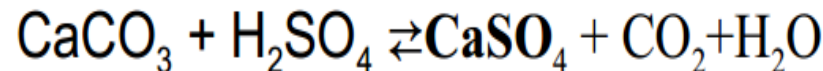
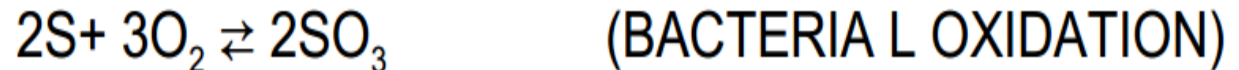
Rn. of the ammendments:

(Case 1: do not have alkaline earth carbonate but high pH)

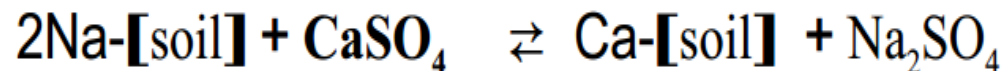
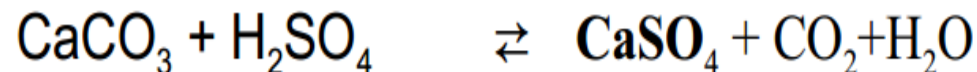
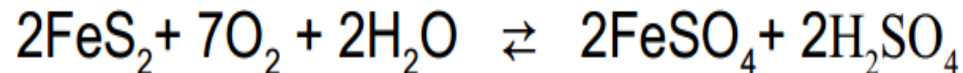


(case 2: have alkaline earth carbonate and high pH)

a) Use of Sulphur:



b) **Use of Iron pyrites; (cheap, indigenous)**



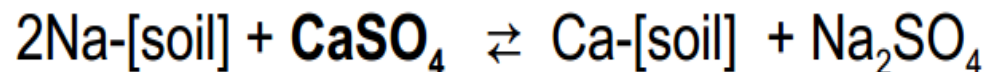
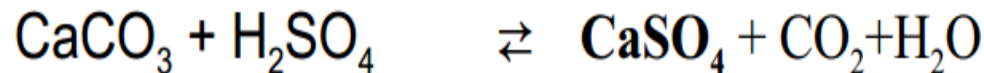
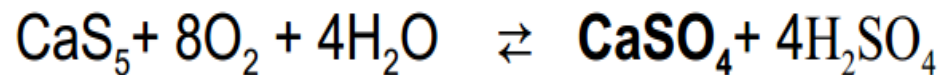
Thiobacillus ferrooxidans,



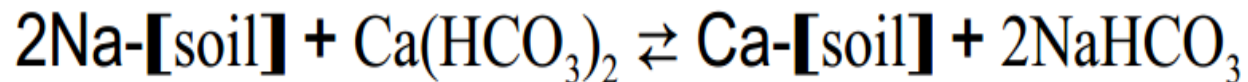
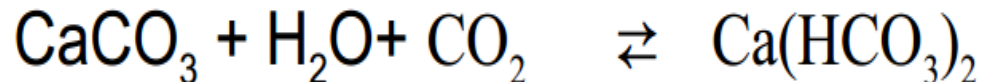
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c) Use of Lime sulphur (by-pdt. of Sugar industry):



(Case 3: do not have alkaline earth carbonate but low pH)





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The exchangeable sodium status of soils can be predicted quite well from the SAR and a Gapon-type exchange equation:

$$\text{ESR} = \frac{[\text{NaX}]}{[\text{CaX} + \text{MgX}]} = \frac{K_G[\text{Na}^+]}{[\text{Ca}^{2+} + \text{Mg}^{2+}]^{1/2}} = K_G \text{SAR}$$

where ESR is the *exchangeable sodium ratio* of the soil, X is the soil, the exchangeable ion concentrations are in millimoles(+) per kilogram, and K_G is the Gapon exchange constant. The range of K_G is commonly 0.010 to 0.015 (L mmol)^{-1/2}. The values of ESR of the soils and ESP/100 (*exchangeable sodium percentage*) of the irrigation water are approximately equal for many irrigated soils at ESP values below 25 or 30% . The exact relation between the two parameters is

$$\text{ESP} = \frac{100 \text{ ESR}}{1 + \text{ESR}}$$

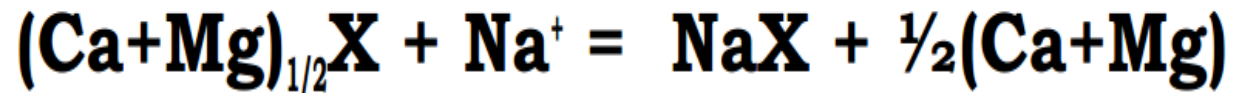


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Use of Ion Exchange Theory to predict the long-term effect of irrigation water on soils

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



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

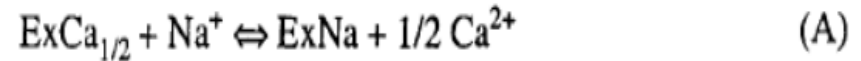


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DERIVATION OF THE EMPIRICAL SAR-ESP RELATIONSHIP

The equation most commonly used to describe heterovalent cation exchange, such as $\text{Na}^+ - \text{Ca}^{2+}$ exchange, is the Gapon exchange equation. For example,



and

$$K_G = [\text{ExNa}/\text{ExCa}_{1/2}][\text{Ca}^{1/2}/\text{Na}] \quad (\text{B})$$

Equation B can be rearranged to solve for ESR:

$$\text{ESR} = \text{ExNa}/\text{ExCa} = K_G(\text{SAR}) \quad (\text{C})$$

where $\text{SAR} = \text{Na}/\text{Ca}^{1/2}$ $[(\text{mmol L}^{-1})^{1/2}]$, K_G is the Gapon exchange selectivity coefficient $[(\text{mmol L}^{-1})^{-1/2}]$, and Ex_i denotes exchangeable cation i (meq 100 g^{-1} soil).

Equation A can be used to solve for ExNa:

$$\text{ExNa} = K_G(\text{CEC})(\text{SAR})/[1 + \text{SAR } K_G] \quad (\text{D})$$

and

$$\text{ESP} = \text{ExNa}/\text{CEC} \times 100 = 100 \cdot K_G(\text{SAR})/[1 + \text{SAR} \cdot K_G] \quad (\text{E})$$

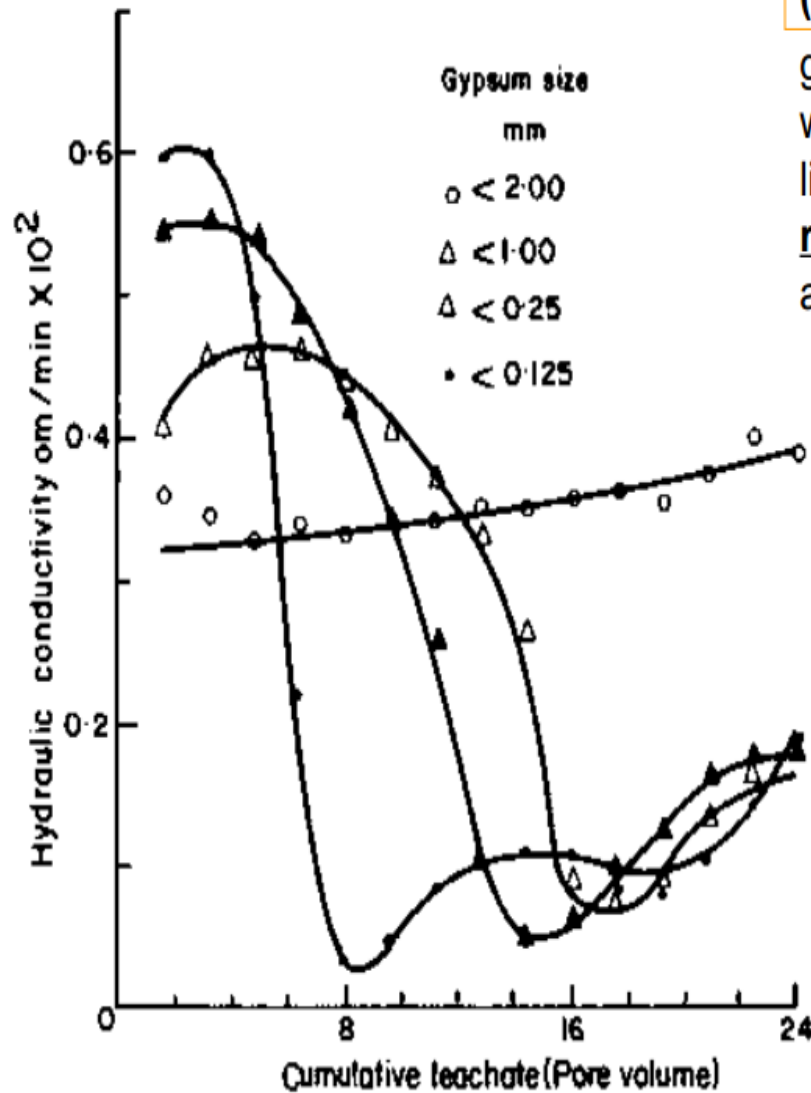
Substituting $\text{SAR} \cdot K_G$ (Equation E) with ESR (Equation C) gives $\text{ESP} = (100)\text{ESR}/[1 + \text{ESR}]$



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Gypsum fineness and solubility



Hydraulic conductivity of a highly sodic soil as affected by gypsum fineness (

Limited solubility of gypsum in water (0.25 percent at 25°C)

gypsum passed through **2 mm sieve** and with a wide particle size distribution was likely to **be more efficient for the reclamation** of sodic soils having appreciable quantities of Na_2CO_3 .

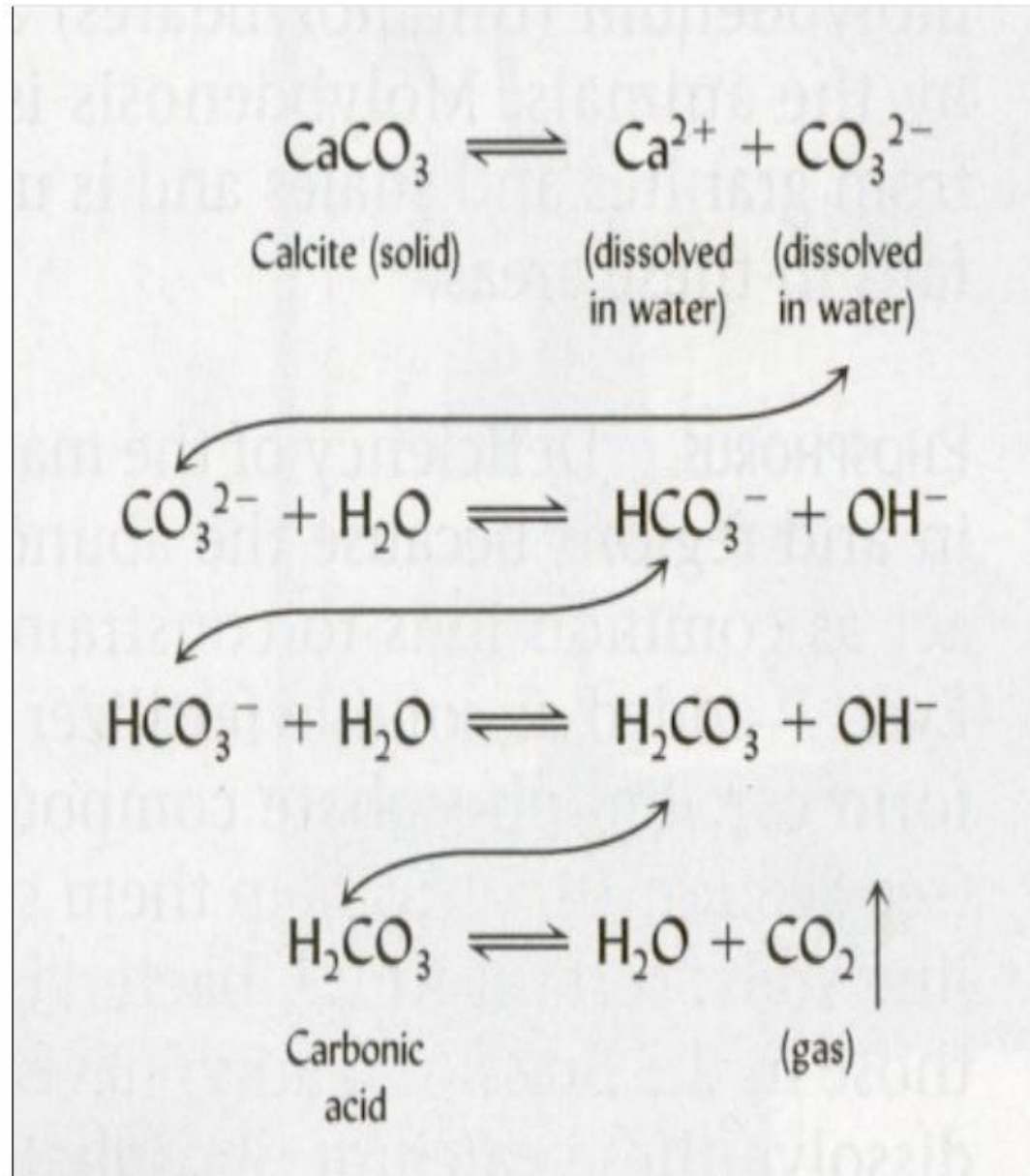
When **gypsum** is mixed in a highly sodic soil **its solubility increases** several fold because of the **preference of exchange sites for divalent calcium ions compared to sodium ions**. The higher the degree of sodium saturation the greater will be the dissolution of gypsum mixed in soil.

Hira et al. (1980) observed that under **14 cm water** were required to dissolve gypsum applied at **12.4 tonnes per hectare** and leach the reaction products from the surface 15 cm soil in a **highly sodic soil (ESP 94.0)**.



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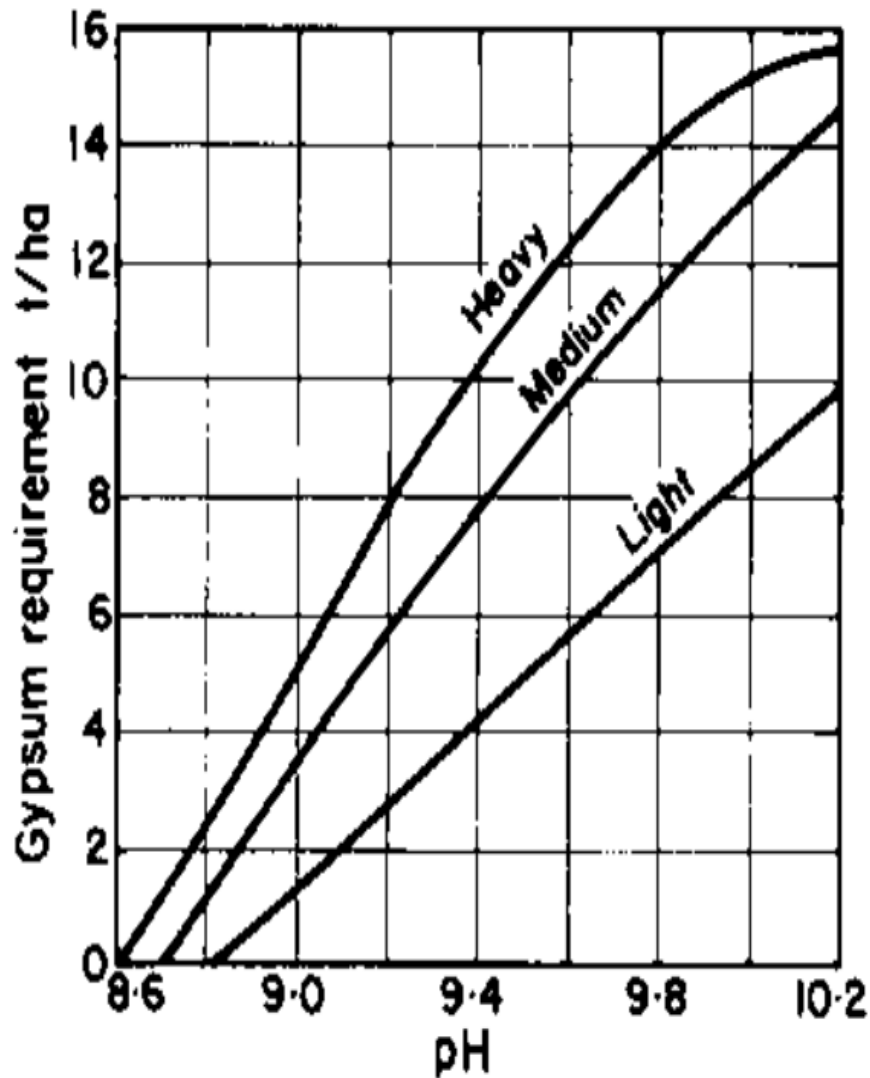


Hydroxyl generating anions carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) from calcite of carbonic acid react with water to form OH ions, thus increase pH



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Relationship between pH of 1:2 soil-water suspension and the gypsum requirements of sodic soils of the Indo-Gangetic plains. Light, medium and heavy refer to soils with a clay content of approximately 10, 15 and 20 percent, respectively. A cation exchange capacity of 10 cmol (+)/kg soil is common for most medium textured soils



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EQUIVALENT QUANTITIES OF SOME COMMON AMENDMENTS FOR SODIC SOIL RECLAMATION

Amendment	Relative quantity
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	1.00
Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)	0.85
Sulphuric acid (H_2SO_4)	0.57
Iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)	1.62
Aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)	1.29
Sulphur (S)	<u>0.19</u>
Pyrite (FeS_2) - 30% sulphur	<u>0.63</u>
Calcium polysulphide (CaS_5) - 24% sulphur	<u>0.77</u>

These quantities are based on 100 percent pure materials. If the material is not 100 percent pure necessary correction must be made. Thus if gypsum is only 80 percent pure the quantity to be added will be $1.00 \times \frac{100}{80} = 1.25$ tons instead of 1.00 ton



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Q. Suppose 0-15 cm layer of an alkali soils contain 4 meq of exch Na/100 g soil and has a CEC of 10 meq/100g . It is desire to reduce the ESP to about 10. Calculate the theoretical amount of gypsum to be applied/ha of land

A. Initial ESP= (Exch Na/CEC)*100= (4/10)*100= 40 meq /100g

B. Final ESP= 10 meq/100 g

C. GR= (ESP_i-ESP_f)*CEC/100= (40-10)*10/100=3 meq/ 100 g

1 meq of Ca will replace 1 meq of Na⁺

3 meq of Ca 3 meq of Na⁺

Eq. wt of Ca= atomic wt/ valency = 40/2= 20

1 meq of Ca = 20 mg of Ca

3 x 20= 60 mg of Ca will be required per 100 g soil

CaSO₄, 2H₂O = 40+32+64+36 =172 g CaSO₄

40 mg Ca is coming from 172 mg Gypsum

60 mg Ca will come from172x60/40 mg gypsum

172x60/40 mg gypsum is required for 100 g soil

For 1000 g(1 kg) soil gypsum will be (172*60/40)*(1000/100) mg

2*10⁶ kg soil need gypsum of amount = 2x 10⁶ (172*60/40)*(1000/100)mg

$$= 2 \times (172 \times 6 / 4) \times 10 \text{ kg}$$

$$= 5160 \text{ kg} = 51.6 \text{ q} = 5.16 \text{ t}$$

Theoretical value of gypsum x 1.2 = Actual value



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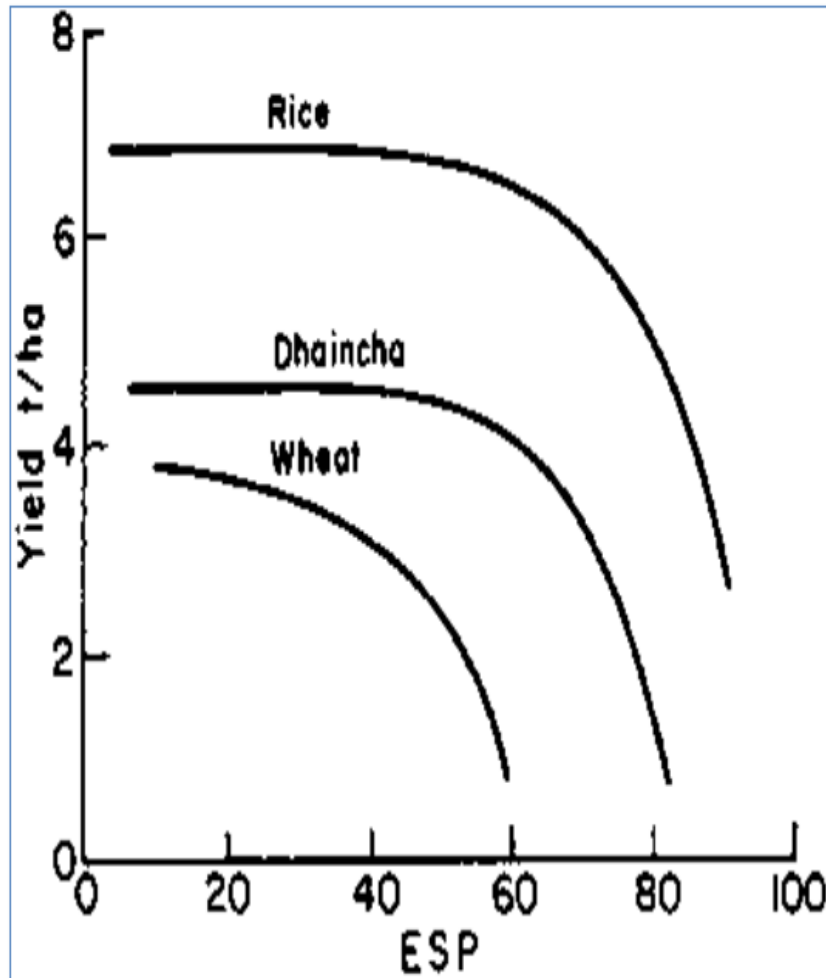
Management strategies

- i) Bulky organic manure, green manure, crop residues and other biological materials which produce weak organic acids help in creating temporarily in acidic condition and help in reclamation
- ii) Leaching with good quality water (low SAR) must follow the application of the reclaiming materials
- iii) A good crop rotation is an excellent insurance agt. Sodicity problem ; rice-dhaincha; Dhaincha-rice-berseem is good
- iv) Frequent irrigation with small quantities of water is the successful irrigation management practices
- v) Sometimes, permeability of soil can increase by deep ploughing

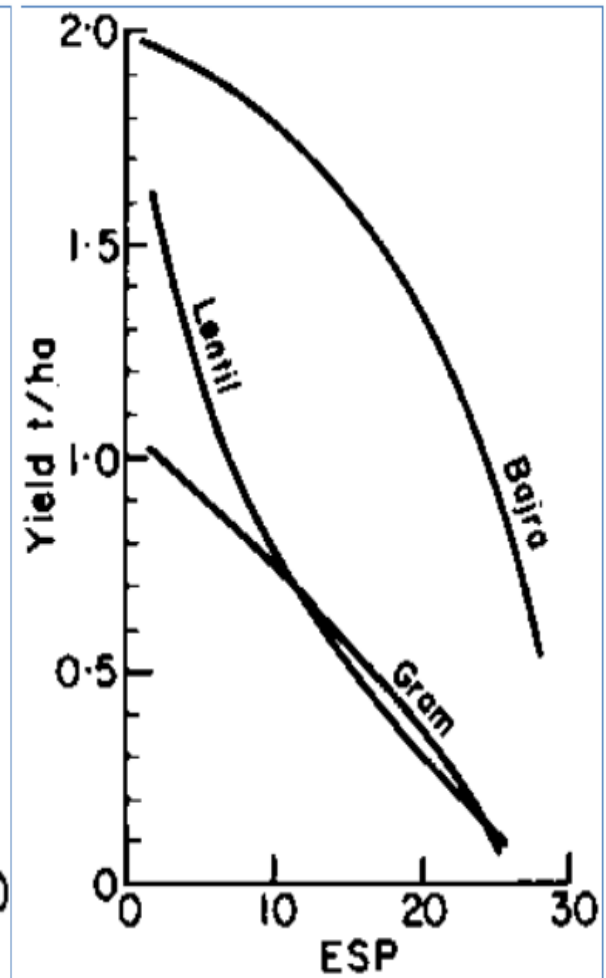


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Relationship between, **ESP and the yield of selected crops** (Abrol and Bhumbra, 1979)



Relationship between exchangeable sodium percentage (ESP) and the yield of selected crops (Abrol and Bhumbra, 1979)



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Quality of irrigation water

Factors on which the quality of irrigation water depends

i) T.D.S (Total dissolved solid) : less than 1000 mg/L

ii) T.S.S (Total Soluble salt): measured by EC

Class-1: C_1 : EC : 0-0.250 mmhos/cm -----safest quality of irrigation

Class-2: C_2 : EC : 0.250-0.750 mmhos/cm ...semi salt tolerant crop

Class-3: C_3 : EC : 0.750- 2.250 mmhos/cm.high salt tolerant, poor quality

Class-4: C_4 : EC : > 2.250 mmhos/cm..... Unsuitable

iii)Relative proportion of Na as compared to Ca and Mg..SAR

S_1 : 0-10, Low

S_2 : 10-18, Medium

S_3 : 18-26, High



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Residual Sodium Carbonate

iv) Relative proportion of CO_3^{2-} and HCO_3^{-} as compared to Ca^{2+} and Mg^{2+}RSC

Measure excess alkalinity in irrigation water

Eaton (1950) suggested that Residual Sodium Carbonate (RSC)

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

High concentrations of bicarbonate and carbonate ions in irrigation water can induce precipitation of calcium and magnesium ions to form calcium and magnesium carbonates, which have low solubility. The precipitation of calcium and magnesium allows sodium ions to dominate and, thus, increases the sodium hazard associated with the irrigation water.



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Rating chart of RSC

0-0.25 (meq/L)	safe
0.25-0.50	medium
0.5-1.5	High
1.5-2.5	Very high
>2.5	unsuitable

A negative RSC indicates that sodium buildup is unlikely since sufficient calcium and magnesium are in excess of what can be precipitated as carbonates. A positive RSC indicates that sodium buildup in the soil is possible.

The RSC value can be used to calculate the amount of gypsum to add per acre-foot of irrigation water to neutralize residual carbonates (i.e., to reduce RSC to 0). This can be calculated using the formulas:

$$\text{RSC} * 234 \text{ lbs. gypsum/acre-foot}$$



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The **SAR** is defined as ratio of the sodium (Na) to the square root of the (Ca + Mg), i.e.:

$$SAR = \frac{Na}{\sqrt{Ca + Mg}} \quad (1a)$$

where all cation measurements

are expressed in milli moles per liter (mmol/L).

Alternatively, if the cation measurements are expressed in milli equivalents per liter (meq/L), then the SAR is defined to

be:

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}} \quad (1b)$$

The standard SAR formulas (eqs. 1a or 1b) represent a suitable sodium hazard index for typical irrigation waters.

However, when waters having appreciable concentrations of calcium (Ca) and/or bicarbonates (HCO₃) are employed for

irrigation, a variable fraction of this constituent will

precipitate in the soil as $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$ (2)

CaCO₃ according to the eqn:



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➤ For high calcium and/or bicarbonate waters (primarily groundwater at elevated CO₂ content), many soil scientists recommend that an adjusted SAR formula be used in place of equations 1a or 1b.

➤ Various adjustments have been proposed in the literature (Bower et al., 1968; Rhoades, 1968; Suarez, 1981). The formula derived by Suarez (1981) is generally recognized as the most applicable technique for determining the adjusted SAR hazard index;

adjusted SAR (adj.SAR), which describes Na⁺ potential in a CaCO₃ saturated solution to influence SAR. It is estimated as follows:

$$\text{adj.SAR} = (\text{SAR}) [1 + (8.4 - \text{pH}_c)]$$

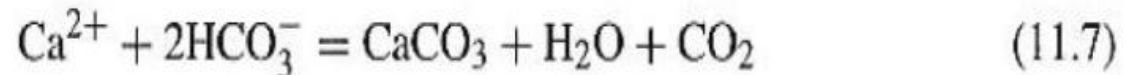


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11.2.2 Bicarbonate Hazard

Another property related to the sodium hazard of irrigation waters is the bicarbonate concentration. Bicarbonate toxicities associated with some waters generally arise from deficiencies of iron or other micronutrients caused by the resultant high pH. Precipitation of calcium carbonate from such waters,



lowers the concentration of dissolved Ca, increases the SAR, and increases the exchangeable-sodium level of the soil. The CaCO_3 precipitation can be accounted for by the adjusted SAR:

$$\text{Adjusted SAR} = \text{SAR} \times [1 + (8.4 - \text{pH}_c)] \quad (11.8)$$

Several workers have characterized the bicarbonate levels of waters with the Langelier Index (LI):

$$\text{LI} = (\text{pH}_a - \text{pH}_c) = \text{pH}_a - (\text{p}K'_2 - \text{p}K'_c) + \text{p}C_a + \text{pAlk} \quad (11.14)$$



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Alkalinity in brines can be evaluated through the use of the **pH_c**. The mathematical expression for the pH_c (Langelier or saturation index) is as follows:

$$\text{Saturation index} = \text{pH} - \text{pH}_c$$

where pH denotes measured-solution pH,

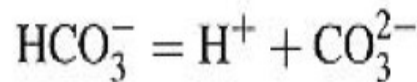
pH_c denotes equilibrium pH for CaCO₃ under a given set of conditions

(under a pCO₂ of 0.0003 and pure CaCO₃, pH_c = 8.4).

When the saturation index >0, CaCO₃ precipitation is expected; when the saturation index <0, CaCO₃ dissolution is expected.

The saturation index can be derived by estimating pH_c as follows:

$$K_{sp} = (\text{Ca}^{2+})(\text{CO}_3^{2-}) = 10.0^{-8.34} \quad (11.7)$$



$$K_2 = \frac{(\text{H}_c^+)(\text{CO}_3^{2-})}{(\text{HCO}_3^-)} = 10.0^{-10.33} \quad (11.8)$$

where *K_{sp}* is the solubility product constant of CaCO₃, *K₂* is the second dissociation constant of H₂CO₃, and the parentheses denote solution ion activity. Rearranging and substituting Equation 11.7 into Equation 11.8 gives

$$K_2 = \frac{(\text{H}_c^+)(K_{sp}/\text{Ca}^{2+})}{(\text{HCO}_3^-)} = 10.0^{-10.33} \quad (11.9)$$



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$$K_2 = \frac{(H_c^+)(K_{sp}/Ca^{2+})}{(HCO_3^-)} = 10.0^{-10.33} \quad (11.9)$$

Taking logarithms on both sides of Equation 11.9 gives

$$-\log K_2 = -\log H_c^+ - \log K_{sp} + \log Ca^{2+} + \log HCO_3^- \quad (11.10)$$

Rearranging,

$$pH_c = pK_2 - pK_{sp} + pCa^{2+} + pHCO_3^- \quad (11.11)$$

A practical approach to estimating the **pH_c of water moving through soil is as follows:**

$$pH_c = (pK'_2 - pK'_c) + p(Ca + Mg) + pAl_k \quad (11.12)$$

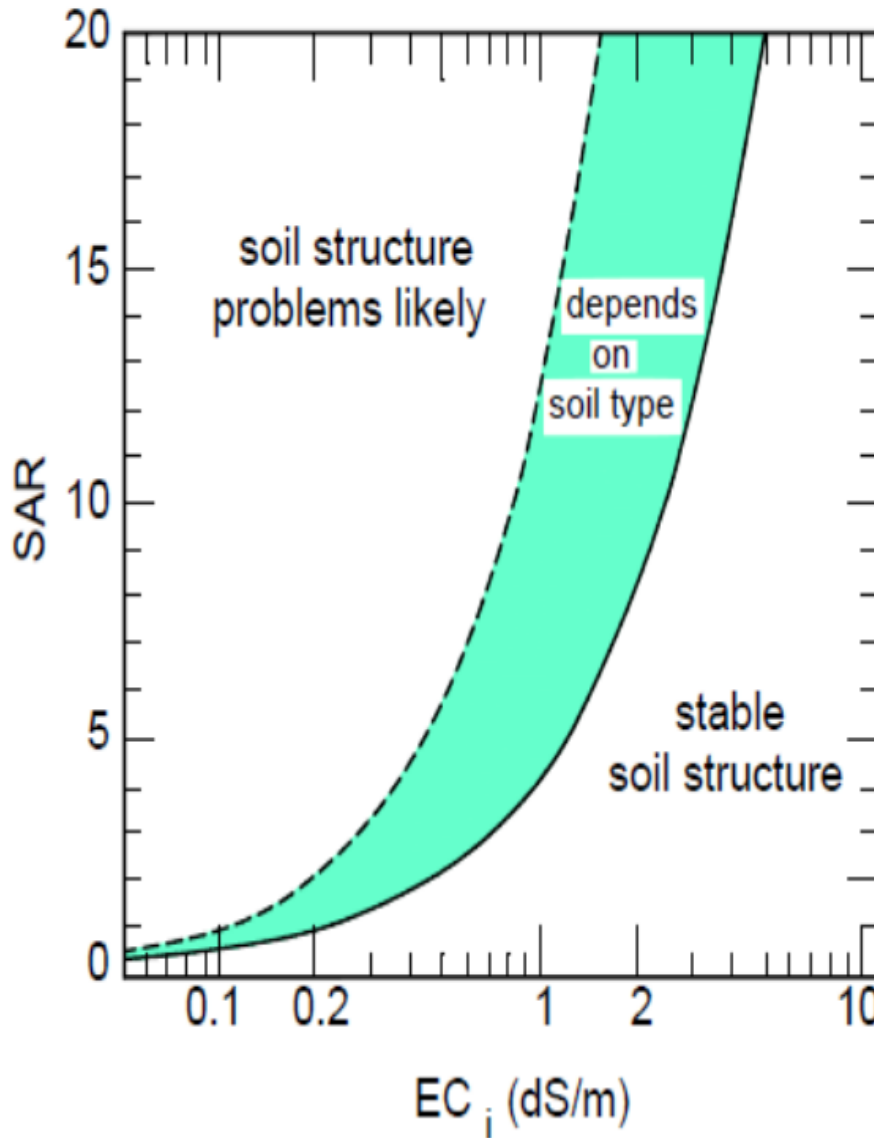
where pK'_2 and pK'_c represent pK_2 and pK_c ($pK'_c = pK_{sp}$) corrected for ionic strength. An estimated pH_c (using Eq. 11.12) of less than 8.4 suggests that Ca^{2+} will precipitate as limestone ($CaCO_3$).

An estimated pH_c (Eqn 11.12) of greater than 8.4 suggests that $CaCO_3$, if present, will dissolve



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water quality that falls to the right of the coloured area is considered satisfactory for use, while values to the left are considered unsatisfactory and special irrigation management will be required. Values that fall between the lines (indicating marginal water quality) should be treated with caution.

Figure 1—Relationship between SAR and EC_i of irrigation water for prediction of soil structure stability



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v) Boron concentration: (ppm)

Boron class	Sensitive crop	Semi tolerant	Tolerant
I	< 0.33	< 0.67	< 1.0
II	0.33-0.67	0.67-1.33	1.0-2.0

Some empirical relationships to be remembered

O.P. (osmotic potential) = -0.36 EC

Total cations (mmoles/L) = EC (dS m⁻¹) x 10

TDS (mg L⁻¹) = EC (dS m⁻¹) x 640



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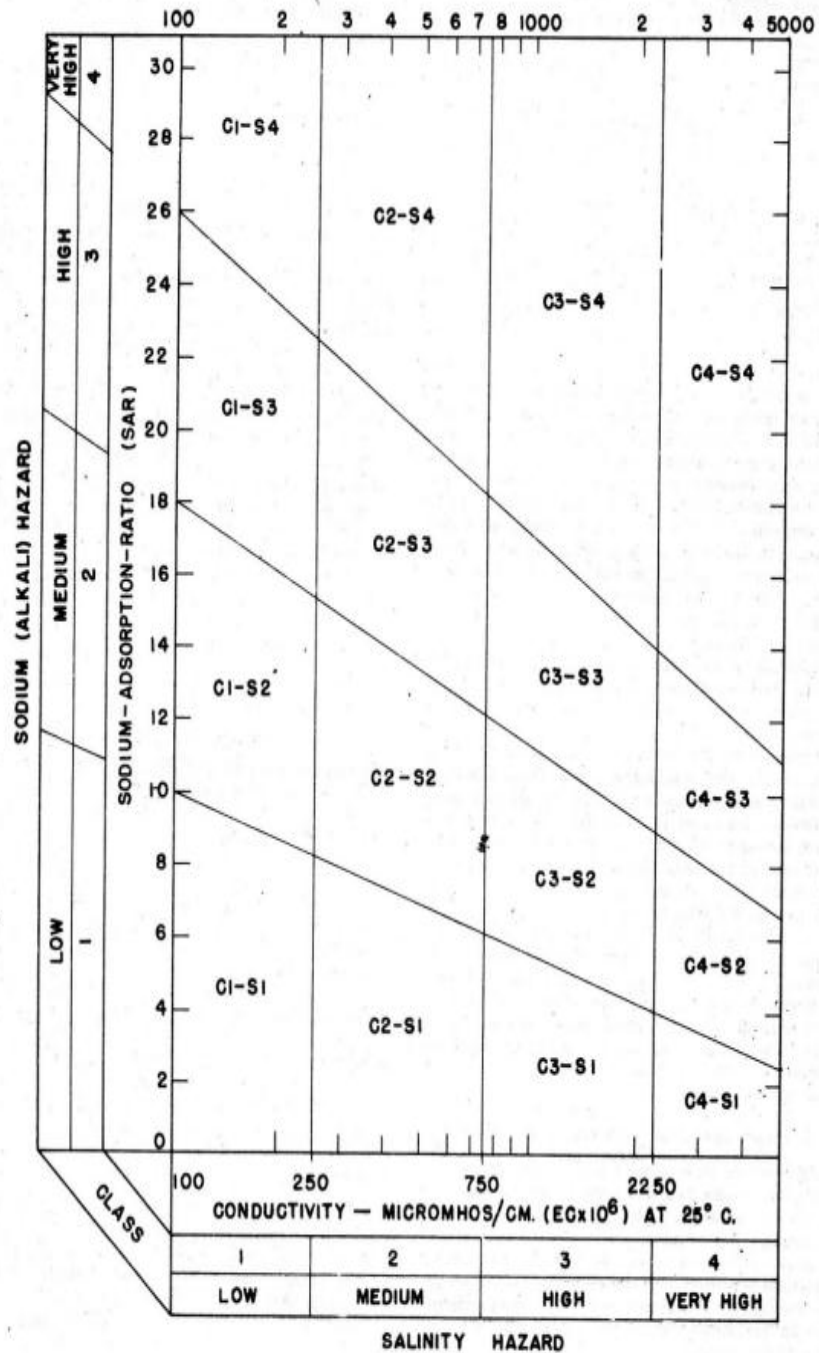


FIGURE 25.—Diagram for the classification of irrigation waters.



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Q. An irrigation water has the following composition:

Ca²⁺..... 60 mg/l

Mg²⁺.....24 mg/l

Na⁺.....69 mg/l

Calculate : a) Concentration of total cations (meq.L)

b) Approximate EC of the water in micromhos/cm

c) TDS in mg/l

d) Osmotic potential in Bar

A. Ca²⁺..... 60 mg/l = 60 /((40/2))= 3 meq/l

B. Mg²⁺.....24 mg/l =24/(24/2)= 2 me/l

C. Na⁺.....69 mg/l = 69/(23/1)= 3 meq/l

Total cations = 3+2+3 = 8 meq/l

Total cations(meq/l)= ECx 10

EC = (3+2+3)/10 = 0.8 mmhos/cm

TDS = 640 x 0.8 mg/l = 512 mg/l

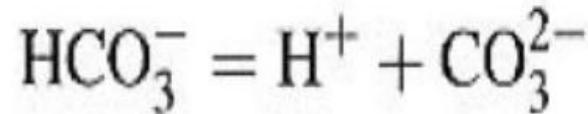
OP = - 0.8x (0.36) bar = -0.288 bar



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where pH_a is the measured pH of the soil or water, pH_c is the calculated pH of the irrigation water if equilibrated with $CaCO_3$, pK'_2 is the second dissociation constant of H_2CO_3 , pK'_c is the solubility product of $CaCO_3$, and pCa and $pAlk$ are the negative logarithms of the molar Ca and molar(+) carbonate plus bicarbonate concentrations, respectively. The pH_c can be derived from the reaction



$$K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)}$$

In a system at equilibrium with solid-phase $CaCO_3$,

$$K_c = (Ca^{2+})(CO_3^{2-})$$

because the activity of solid-phase $CaCO_3$ can be taken as unity. Substituting Eq. 11.17 into 11.16 and rearranging gives

$$(H^+) = \frac{K_2(HCO_3^-)(Ca^{2+})}{K_c} \quad (H^+) = \frac{K_2\gamma_{HCO_3}[HCO_3^-]\gamma_{Ca}[Ca^{2+}]}{K_c}$$

where brackets indicate concentrations and the γ 's are activity coefficients. Taking negative logarithms gives

$$pH_c = pK'_2 - pK'_c + p(\gamma HCO_3) + p(\gamma Ca) + p[PCO_3^-] + p[Ca]$$

Combining the two activity coefficients with the dissociation and solubility constants gives

$$pH = (pK'_2 - pK'_c) + p[HCO_3^-] + p[Ca^{2+}]$$



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Soil clay dispersion

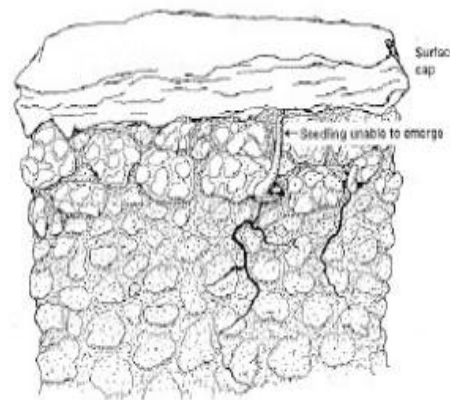
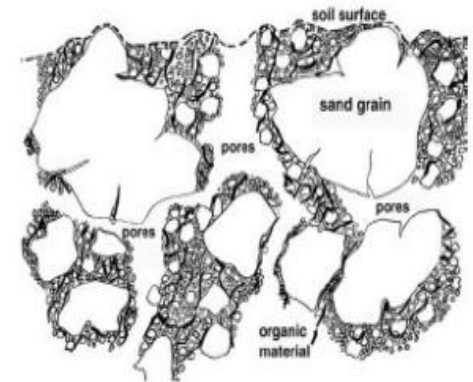
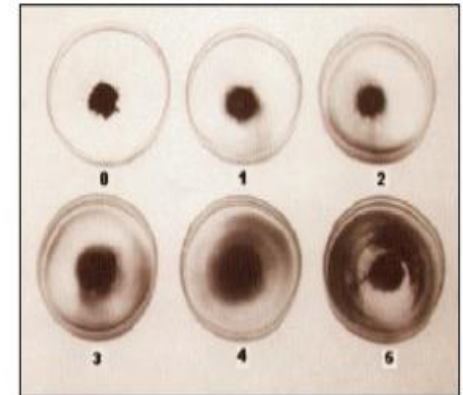
Slaking and aggregate destruction

Reduced macroporosity

Reduced aeration

Reduced percolation

Surface sealing (crusts)



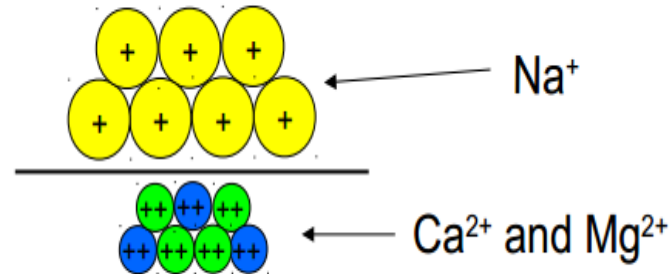


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Sodium Adsorption Ratio

The ratio of 'bad' to 'good' flocculators gives an indication of the relative status of these cations:



Mathematically, this is expressed as the 'sodium adsorption ratio' or SAR:

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

where concentrations are expressed in mmoles/L

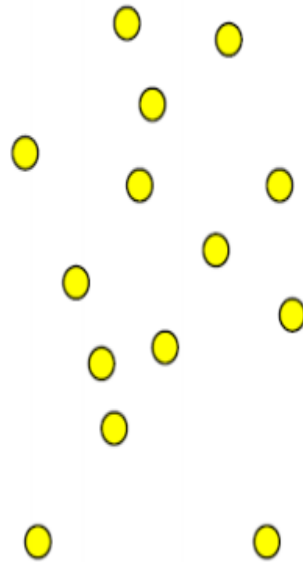


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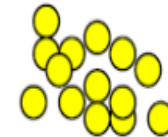
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Soil clay particles can be unattached to one another (*dispersed*) or clumped together (*flocculated*) in aggregates. Soil aggregates are cemented clusters of sand, silt, and clay particles.

Dispersed Particles



Flocculated Particles

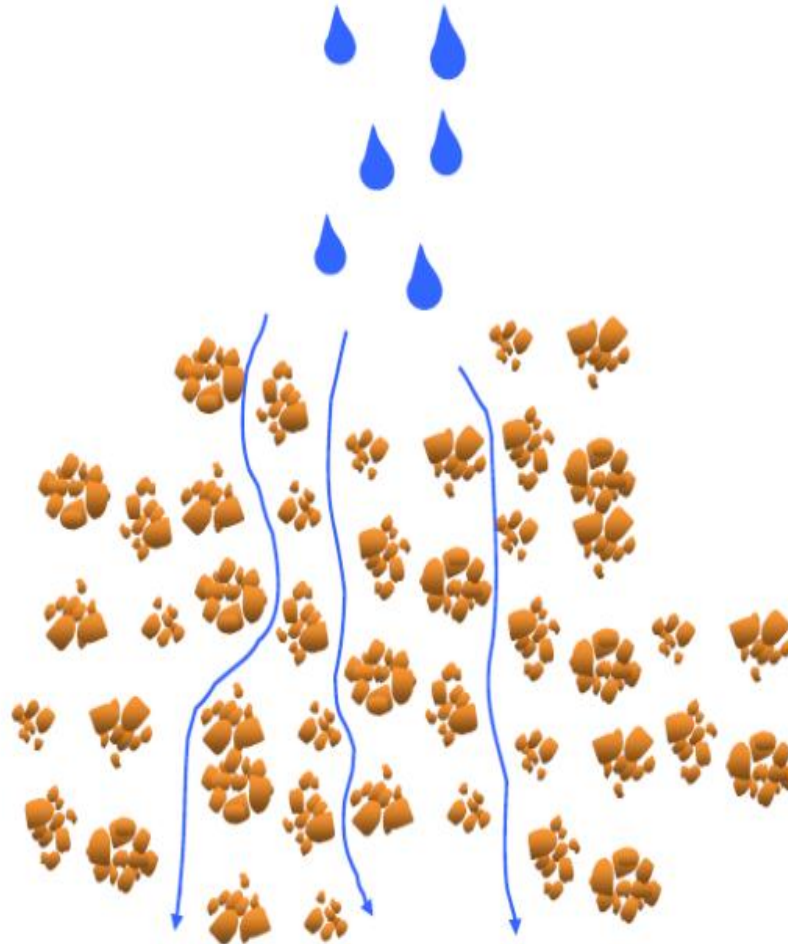




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Flocculation is important because water moves mostly in large pores between aggregates. Also, plant roots grow mainly between aggregates.





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In all but the sandiest soils, dispersed clays plug soil pores and impede water infiltration and soil drainage.

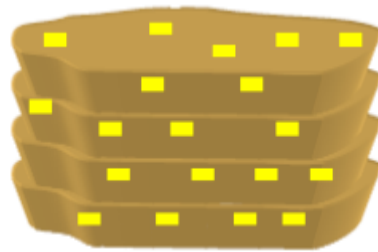




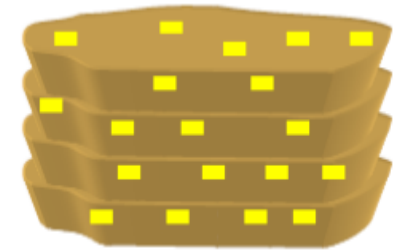
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Most clay particles have a negative electrical charge. Like charges repel, so clay particles repel one another.



Negatively charged
clay particle



Negatively charged
clay particle

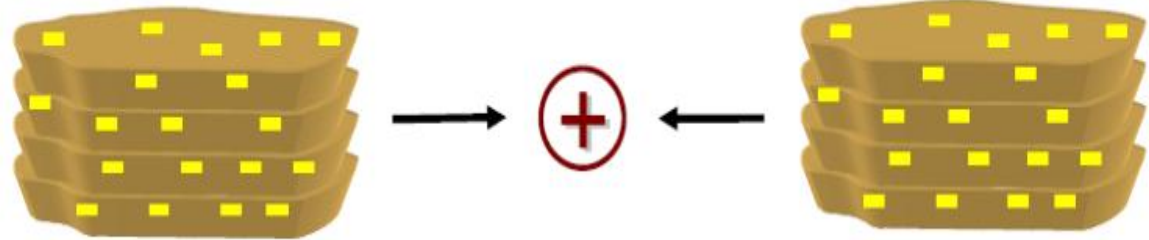


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A cation is a positively charged molecule. Common soil cations include sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}).

Cations can make clay particles stick together (flocculate).



Negatively charged
clay particle

Negatively charged
clay particle

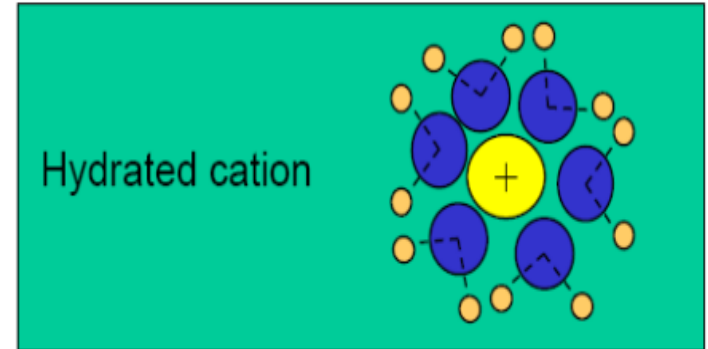
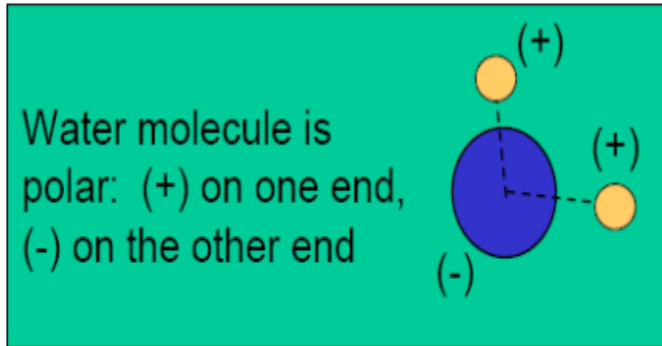


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Flocculating Power of Cations

Cations in water attract water molecules because of their charge, hydrated



Cations with a single charge and large hydrated radii are the poorest flocculators.

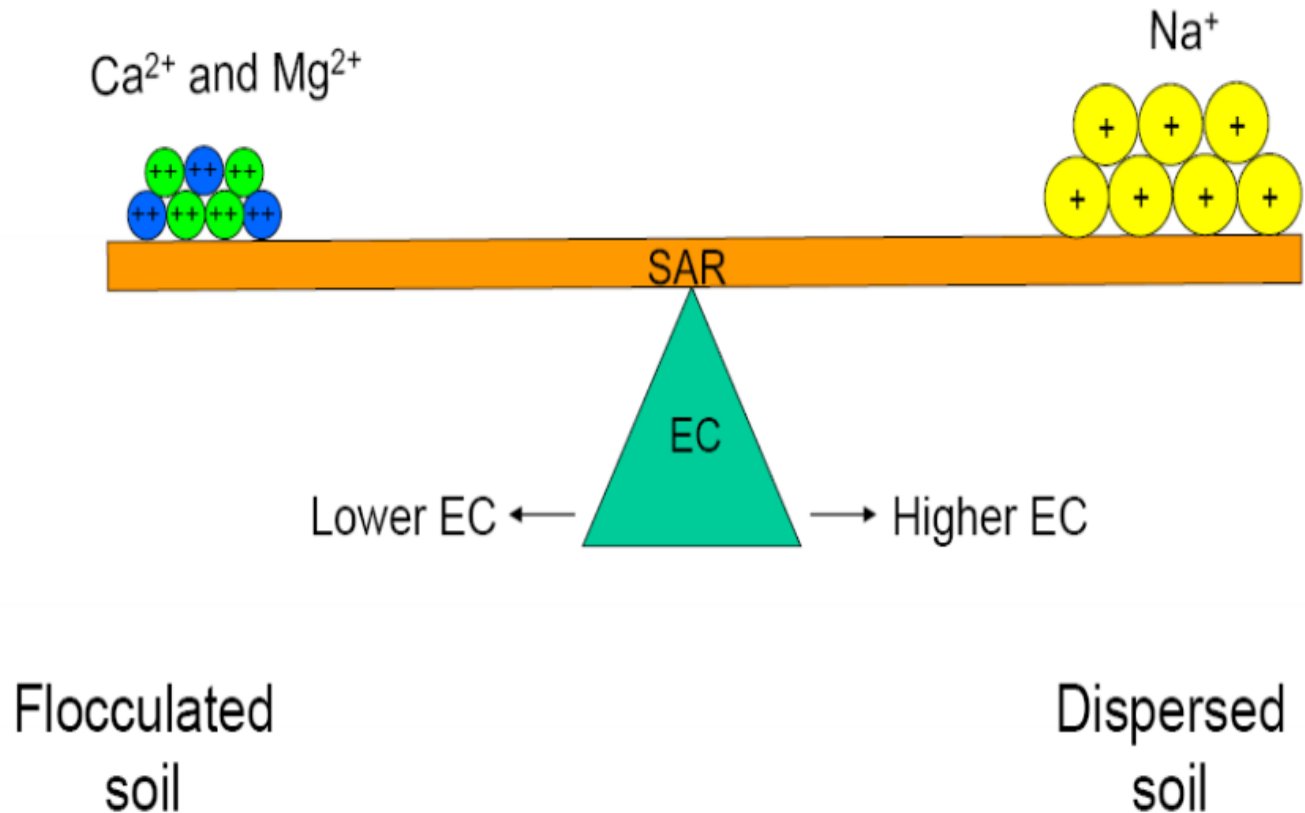
Cation	Charges per molecule	Hydrated radius (nm)	Relative flocculating power
Sodium	1	0.79	1.0
Potassium	1	0.53	1.7
Magnesium	2	1.08	27.0
Calcium	2	0.96	43.0



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Aggregate stability (dispersion and flocculation) depends on the balance (SAR) between (Ca^{2+} and Mg^{2+}) and Na^+ as well as the amount of soluble salts (EC) in the soil.

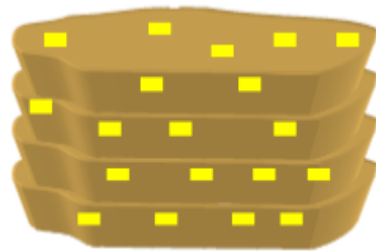




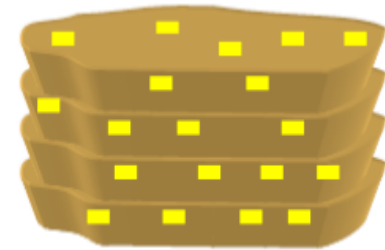
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clay particle



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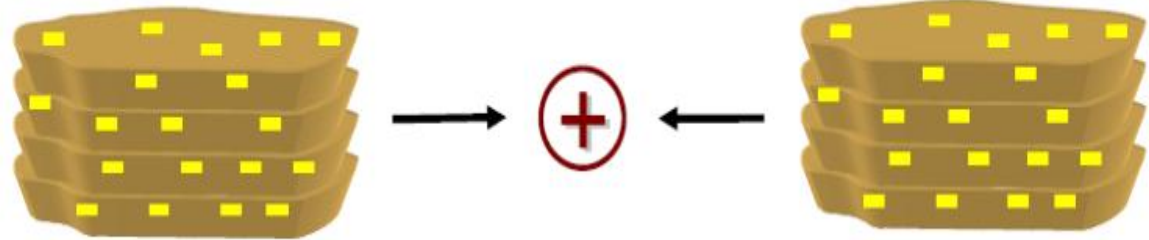


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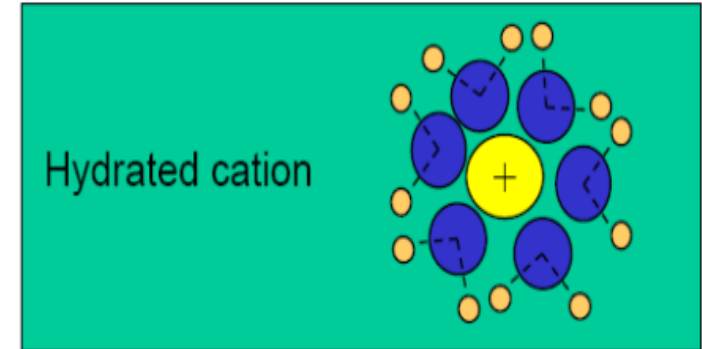
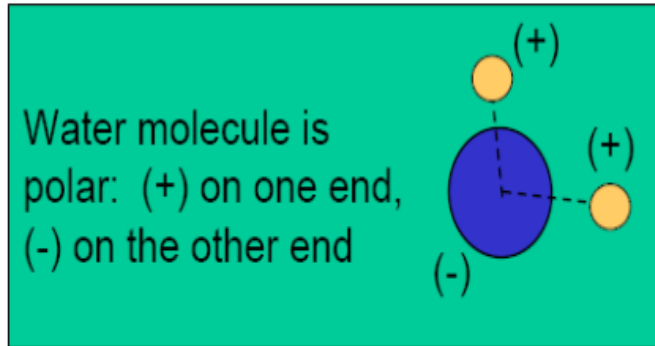


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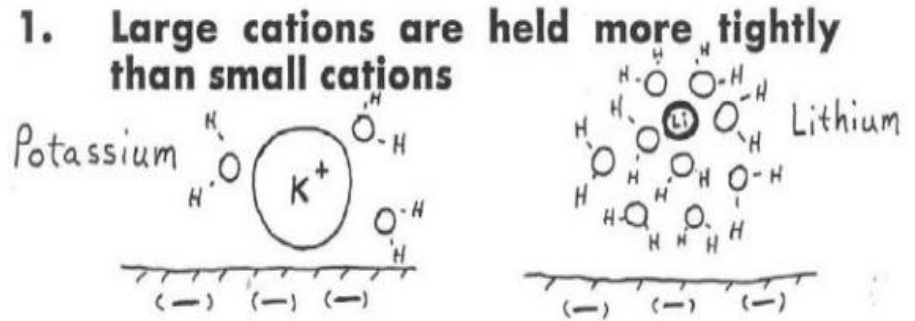


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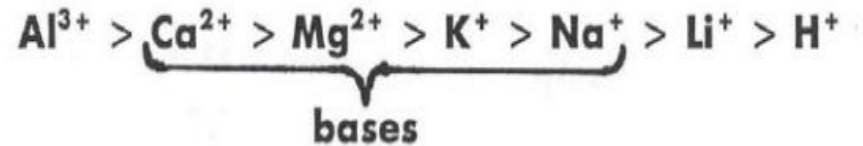
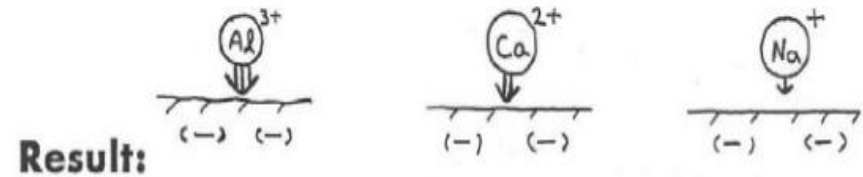
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Rules of Cation Exchange:

Cation Selectivity



Charge Equivalence



Ratio Law

3. **Any one cation can replace any other if its concentration is high enough.**

(MASS-ACTION RULE)

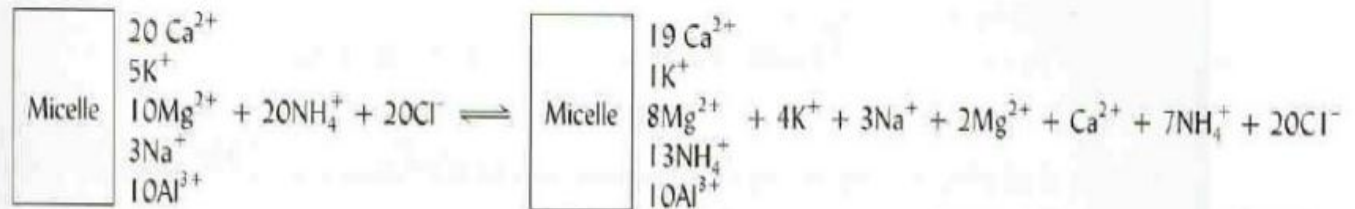
Reversibility = all exchanges are reversible



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Complementary Cations 4. the combined influence of charge equivalencies, ion selectivity and complementary ions drive the exchange of cations



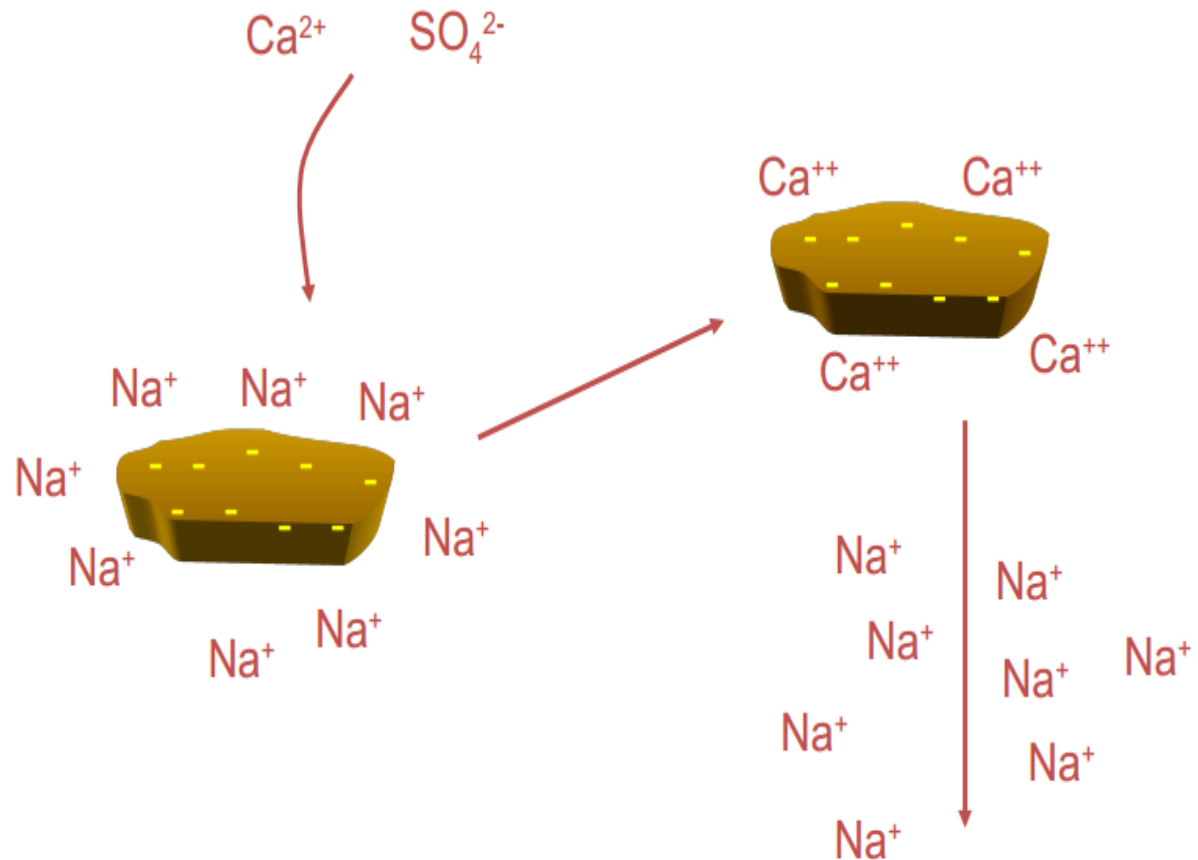
Generally it is the cations with the largest ionic radii and the lowest hydration energies that adsorb most strongly on the permanent charge sites of clay minerals.



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Apply gypsum *before* leaching salts out of soils susceptible to dispersion (the amount of gypsum needed can be determined by a soil test). Replacing sodium with calcium before leaching will stabilize soil structure.



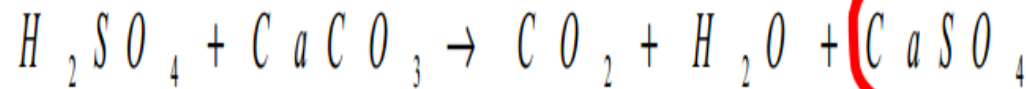


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Sulfuric acid* can be used instead of gypsum on calcareous (CaCO₃ containing) soil only.

- Sulfuric acid dissolves calcium carbonate in the soil



and makes gypsum!

*Sulfuric acid is extremely dangerous and should only be handled by trained personnel.



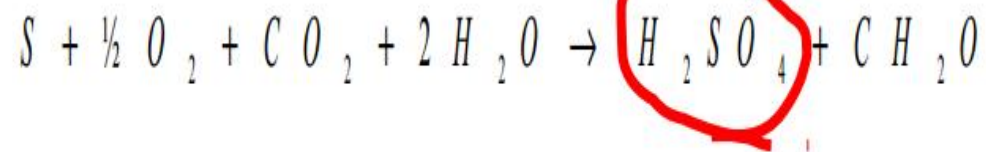
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Elemental sulfur can also be used as an alternative to gypsum on calcareous soils



- Soil microbes convert sulfur into sulfuric acid



– H_2SO_4 dissolves calcium carbonate and makes gypsum

- Conversion to sulfuric acid takes time

- several weeks
- faster in warm soils



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ELECTRICAL DOUBLE LAYER (EDL):

If we put a charged particle in a suspension with ions, then the primary charge will attract counter ions (opposite charged ions) by **electrostatic attraction**. The primary charge cannot attract an equal amount of counter charge because a gradient of counterions is established that drives the counterions away from the surface.



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The formation of the electrical double layer (EDL) then occurs via **attraction of oppositely charged counterions** by the primary surface charge and then a diffusion of the counterions away from the surface. The counterions are mobile, the primary charge is not. The EDL development is schematically shown here:



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As a result of this EDL there is a net electrostatic repulsion/attraction developed between colloids. This net force is shown below:



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The net resultant force is a result of:

1. attractive potential energy (mostly van der Waals forces), V_a . These forces are very strong at short separation distances

2. repulsion potential energy (electrostatic forces), V_R . (by Coulomb's law).

$$V_a \propto \frac{1}{r^6}$$

$$V_R \propto \frac{1}{r^2}$$



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*Shaping Lives...
Empowering Communities...*

The rate of agglomeration of colloids depends on the net resultant force between colloids. The higher the net repulsive force the less effective will be the coagulation. The basic goal of coagulation is to reduce the net repulsive force. We'll discuss ways to do that, but first let's look at ways to quantify the EDL via **Zeta Potential** and Electrophoretic mobility.