EXCHANGE EQUATIONS:

Exchange equations are used for the assessment of the concentration of exchangeable ions from those of soluble ions. In general, a very small part of the total amount of salts is adsorbed by the soil exchange complex. However, this part is very important from plant nutrition point of view and for the determination of some soil properties. There are many approaches on the basis of which exchange equations have been developed between the soluble and the exchangeable ions. These approaches are classified into:

1. Kinetic and Statistical approach
2. Mass action (Gapon equations)
3. Donnan's distribution
4. Diffuse Double Layer Theory
5. Application of Thermodynamics to soils

For the assessment of sodicity hazard on the soil exchange complex (exchangeable Na), the knowledge of soluble Na in terms of SAR can be used by the Gapon equation.

Gapon Equation:

In an ideal nonsaline-nonsodic soil, about 65 % of the cation exchange sites are occupied by Ca, 10 % by Mg, 5 % by K and 20 % by H. Calcium saturated soils are flocculated and permeable to water, while Na saturated soils are generally deflocculated, dispersed and impermeable to water. The excess of Na in irrigation waters may adversely affect soil properties and thus, decrease soil productivity. The Na in irrigation water is one of the major sources that saturate soils with Na. Thus, it becomes necessary to estimate adsorbed Na build up in soils in terms of ESP or SAR of soil solution.

In 1933, Gapon proposed a theory for cation exchange in soils by using a kinetic and mass action approaches. Major features of the Gapon equation include using concentration rather than activities for soluble ions and writing the mass action equation with chemically equivalent quantities both for the exchange sites and the exchange cations. The Gapon equation is one of the simplest of ion exchange equations. Gapon published his equation for Ca-Na exchange as

$$Ca_{1/2}X + Na^{+} \quad = \quad NaX + \tfrac{1}{2}\,Ca^{2+} \qquad 1$$

Where X = exchange complex and cations are as meL^{-1} of soil

Gapon pointed out that Ca^{2+} on exchange sites behaves as does Na^{+} when both cations are expressed in equivalent units which leads to the expression

$$CaX + Na^{+} \quad = \quad NaX + \tfrac{1}{2}\,Ca^{2+} \qquad 2$$

and Gapon coefficient (K_G) is

$$K_G \quad = \quad \frac{(NaX)\,(Ca^{2+})^{1/2}}{(CaX)\,(Na^{+})} \qquad 3$$

In 1954, USDA introduced two terms

$$ESR = NaX / CaX \qquad 4$$

$$SAR = Na^+ / (Ca^{2+})^{1/2} \qquad 5$$

ESR is exchangeable sodium ratio and SAR is sodium adsorption ratio. Later USDA modified the above equations to combine Mg^{2+} with Ca^{2+} due to divalent nature of both cations. Hence,

$$ESR = \frac{NaX}{CaX + MgX} = \frac{NaX}{CEC - NaX} \qquad 6$$

(where cations are in $mmol_c\ 100\ g^{-1}$ in equation 6)

$$SAR = \frac{Na+}{(Ca^{2+} + Mg^{2+})^{1/2}} \quad \text{Conc. In mmol } L^{-1} \qquad 7$$

$$SAR = \frac{Na+}{[(Ca^{2+} + Mg^{2+})/2]^{1/2}} \quad \text{Conc. In mmol}_c\ L^{-1} \qquad 8$$

$$K_G = ESR \frac{1}{SAR} \qquad 9$$

$$K_G .SAR = ESR \qquad 10$$

For a Ca-Na system, exchangeable sodium fraction (ESF) is

$$ESF = \frac{NaX}{CEC} = \frac{NaX}{CaX + NaX} = \frac{NaX / CaX}{(CaX / CaX) + (NaX / CaX)} = \frac{ESR}{1 + ESR} \qquad 11$$

Since $ESR = \frac{NaX}{CaX}$

and $ESR = K_G .SAR$

therefore,
$$ESF = \frac{ESR}{1 + ESR} = \frac{K_G .SAR}{1 + K_G .SAR} \qquad 12$$

But, it is known to us that

$$ESP = \frac{NaX}{CEC} 100 \qquad 13$$

Hence,
$$ESP = 100\ ESF = \frac{100\ ESR}{1 + ESR} \qquad 14$$

ESP is the measure of Na^+ saturation of soil exchange sites and value of ESR has been determined using data of US soils as under:

So $$ESR = -0.0126 + 0.01475\ SAR \qquad 15$$

$$ESP = \frac{100\,(-0.0126 + 0.01475\ SAR)}{1 + (-0.0126 + 0.01475\ SAR)} \qquad 16$$

The value of K_G is 0.01475 while -0.0126 is the Y intercept. However, Franklin & Schmehl (1973) found the value of ESR for soils of Pakistani Punjab as

So $$ESR = 0.0063 + 0.0124\ SAR \qquad 17$$

$$ESP = \frac{100\,(0.0063 + 0.0124\ SAR)}{1 + (0.0063 + 0.0124\ SAR)} \qquad 18$$

By simplifying it will be as

$$ESP = 1.94 + 0.903\ SAR \qquad 19$$

Ghafoor et al. (1988) calculated this relationship for two soils of Pakistani Punjab as

$$ESP = \frac{100\,(-0.0268 + 0.02588\ SAR)}{1 + (-0.0268 + 0.02588\ SAR)} \quad \text{(soil a)} \qquad 20$$

$$ESP = \frac{100\,(-0.0867 + 0.02018\ SAR)}{1 + (-0.0867 + 0.02018\ SAR)} \quad \text{(soil b)} \qquad 21$$

The values of Y intercept and K_G for Pakistan soils are higher most probably due to low CEC and very low organic matter. These modified Gapon equations can be used for predicting the expected exchangeable cation status of a given soil in equilibrium with a given irrigation water. Hence, SAR is used for evaluating sodium status of soils. Some Soil Scientists prefer to use SAR over ESP because of the simplicity and precision involved in analytical work done for SAR determination than for ESP estimation.