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DEVELOPMENT OF THE GAPON EQUATION AND ITS APPLICATION FOR EVALUATING IRRIGATION WATERS AND SOILS

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ABSTRACT

In the published literature of Soil sciences a number of modifications of the Gapon equation have been proposed from time to time. These modifications have been examined in detail and put in the right perspective. The assumptions in this equation and their limitations are discussed.

INTRODUCTION

In considering the physical properties of soils and the mineral nutrition of plants growing on soils, the saturation of exchange sites by various ions and the relations between exchangeable ions and their concentrations in soil solution are of great importance. The equations for relating the distribution of adsorbed ions to solution ions may be classified into several categories. They include the kinetic and statistical approaches, mass action equations, Donnan distribution, double-layer theory and the application of thermodynamics.

The soil tilth depends on the nature of exchangeable cations also. In an ideal soil, 65% of the exchange sites should be occupied by calcium, 10% by magnesium, 5% by potassium and 20% by hydrogen (Toth, 1964). Calcium saturated soils are flocculated and permeable to water, while sodium saturated soils are generally deflocculated, dispersed and impermeable to good quality water. Some other physical properties of soil like swelling and plasticity and the chemical properties like availability of K and other nutrients are affected adversely by the excess of exchangeable sodium. The excess of sodium in irrigation waters may adversely affect soil properties and thus decrease soil productivity.

It is for this reason that an attempt is being made here to review and consolidate different modifications of the Gapon equation since 1933 to-date so that it can be used with more confidence and accuracy for the classification of salt-effected soils and sodic waters. These modifications also help in predicting the effects of irrigation waters on soils more accurately and thus may be helpful in their evaluation for agricultural purposes.

DEVELOPMENT OF THE EQUATION

Gapon (1933) published his equation in Russia and it came to the knowledge of American workers in 1934. Gapon equation is for non-symmetric system. For Ca/Na exchange system he wrote the equation :

$$Ca_{\frac{1}{2}}X + Na^{+} = NaX + \tfrac{1}{2}Ca^{++} \qquad (1)$$

where, X stands for the soil exchange complex. Gapon pointed out that on the soil exchange complex, Ca behaves as does Na when expressed on equivalent basis. This leads to the equation :

$$CaX + Na^{+} = NaX + \tfrac{1}{2}Ca^{++} \qquad (2)$$

In this equation the concentrations of exchangeable cations are expressed in milliequivalents (me) per unit weight of soil e.g., me/100g or me/g and those of cations in the equilibrium solution in millimoles per liter (mmoles/l). For working out the Gapon exchange coefficient it is written as :

$$\frac{(NaX)\ (Ca^{++})^{\frac{1}{2}}}{(CaX)(Na^{+})} = KG \qquad (3)$$

The U. S. Salinity Laboratory Staff (1954) introduced two terms :

$$ESR = \frac{NaX}{CaX} \qquad (4)$$

$$SAR = \frac{Na^{+}}{\sqrt{Ca^{++}}} \qquad (5)$$

where, ESR is the exchangeable sodium ratio and SAR is the sodium adsorption ratio. The U. S. Salinity Laboratory Staff (1954) modified the Gapon equation to include Mg with Ca. This leads to the expressions :

$$ESR = \frac{NaX}{CaX + MgX} = \frac{NaY}{CEC\text{-}NaX} \qquad (6)$$

$$SAR = \frac{Na^{+}}{(Ca^{++} + Mg^{++})^{\frac{1}{2}}} \qquad (7)$$

where,all concentrations are expressed as me per unit weight of soilif the concentrations of solution cations are expressed in mmoles/l. However,

$$SAR = \frac{Na+}{\left(\frac{Ca^{++} + Mg^{++}}{2}\right)^{\frac{1}{2}}} \qquad (8)$$

if the concentrations of solution cations are expressed in me/l. The units of SAR in both the cases come out to be $(mmoles/l)^{\frac{1}{2}}$, while ESR is unitless. Substituting ESR and SAR into equation 3 in becomes :

$$ESR \times \frac{1}{SAR} = KG \qquad (9)$$

where, K_G is the Gapon exchange coefficient. According to Bohn *et al.* (1979), the values of K_G vary from 0.010 to 0.015 $(liters/mmole)^{\frac{1}{2}}$ for most arid zone soils depending upon the surface charge density of the clay minerals and organic matter content. Since the units of cation exchange capacity are me/100 g and those of surface area are $cm^2/100g$, therefore, the unit of surface charge density comes out as me/cm^2. In other words, the surface charge density is the CEC/ unit area. As the surface charge density increases, the polyvalent cations are preferably adsorbed and the value of K_G decreases and vice versa. Bower (1959) found that for a Na-Ca-Mg-K system, the equilibrium between Na and

Ca + Mg is largely independent of K (potassium). From now on, for simplicity, K will be used in place of K_G. Simplifying the equation No. 9, we get

$$\mathrm{KSAR} = \mathrm{ESR} \qquad (10)$$

For a Ca/Na system, the exchangeable sodium fraction (ESF) in equal to :

$$\mathrm{ESR} = \frac{\mathrm{NaX}}{\mathrm{CEC}} = \frac{\mathrm{NaX}}{\mathrm{CaX} + \mathrm{NaX}} = \frac{\dfrac{\mathrm{NaX}}{\mathrm{CaX}}}{\dfrac{\mathrm{CaX}}{\mathrm{CaX}} + \dfrac{\mathrm{NaX}}{\mathrm{CaX}}} \qquad (11)$$

since $\mathrm{ESR} = \dfrac{\mathrm{NaX}}{\mathrm{CaX}}$ and ESR = KSAR, therefore

$$\mathrm{ESF} = \frac{\mathrm{ESS}}{1+\mathrm{ESR}} = \frac{\mathrm{KSAR}}{1+\mathrm{KSAR}} \quad \text{and} \qquad (12)$$

$$\mathrm{ESP} = 100\ \mathrm{ESF} = \frac{100\ \mathrm{KSAR}}{1+\mathrm{KSAR}} \qquad (13)$$

The exchangeables sodium percentage (ESP) is a measure of sodium saturation of the soil exchange comlex. On page 26 of Handbook 60, the U. S. Salinity Laboratory Staff (1954) have written the equation :

$$\mathrm{ESP} = \frac{100(-0.0126 + 0.01475\ \mathrm{SAR})}{1 + (-0.0126 + 0.01475\ \mathrm{SAR})} \qquad (14)$$

For many arid zone soils of Western States the U.S. Salinity Laboratory Staff found that

$$\mathrm{ESR} = -0.0126 + 0.01475\ \mathrm{SAR} \qquad (15)$$

where 0.01475 is the value of Gapon exchange coefficient and -0.0126 is the value of Y intercept. However, Franklin and Schmehl (1972) worked out the following regression equation for Pakistan soils :

$$\text{ESR} = 0.0063 + 0.0124\ \text{SAR} \qquad (16)$$

The intercept in this linear regression equation is slightly higher for the Punjab soils than for the U.S. soils but the slope is lower. The lower slope of equation 16 indicates less sodium hazard from a given water for the Punjab soils in which hydrous mica (illite) and chlorite clay minerals dominate. Either the equation :

$$\text{ESR} = 1.94 + 0.903\ \text{SAR} \ \text{(Franklin and Schmehl, 1973).} \qquad (17)$$

or

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

should give improved estimates of ESR for Pakistan soils. The SAR is useful for predicting the expected exchangeable cation status or expected ESP of a given soil in equilibrium with a given irrigation water. Hence, the SAR is one of the parameters used for classification of irrigation waters and for evaluating the sodium status of soils. Some authors (Bohn *et al.*, 1979) prefer the use of SAR over ESP.

It is implicitly given in the Gapon equations that SAR depends upon the concentration of salts in the irrigation water or soil solution. If the concentration of salts in solution increases 4 times, without any change in the relative ratio of Na : (Ca + Mg), the SAR is doubled. Conversely, if the salt concentration is decreased by a factor of 4 by dilution, the SAR of the diluted water will be equal to half of that of the original water. This is called the 'valence dilution' principle (Eaton and Sokoloff, 1935). This principle of decrease in SAR with dilution has been made use by Reeve and Bower (1960); Reeve and Doering (1666) and Muhammed *et al.* (1909) for reclaiming slowly permeable and fine-textured sodic soils by high-salt water dilution method. In addition to chemically reclaiming the soil, the use of high-salt waters also helps in maintaining or increasing the soil hydraulic conductivity. For predictive purposes, the ESR is given by the equation :

$$ESR = K\ SAR_{ss} \qquad (19)$$

where, SARss is the SAR of the soil solution. It is assumed that SAR of the soil solution (SAR_{ss}) is not the same as that of the irrigation water. SAR of the soil solution is mostly higher than that of the applied irrigation water due to its concentration through water absorption by plants, evaporation from soil surface and dissolution of salts from soil particles. The concentration of soil solution is generally 2 to 10 times greater than that of irrigation water. Under very adverse conditions, concentration of soil solution may be even 50-100 times greater than that of the irrigation water. When increase in the concentration of irrigation water, as a result of evapotranspiration and dissolution, is taken into consideration, the equation becomes :

$$ESR = K\ SAR_{iw} \sqrt{C} \qquad (20)$$

where, C is to equal to concentration factor and SAR_{iw} is the SAR of irrigation water. The SAR of drainage water (SAR_{dw}) is approximated by the equation:

$$SAR_{dw} = SAR_{ss} = SAR_{iw} \sqrt{C} \qquad (21)$$

After the irrigation water enters the soil, its concentration increases due to evapotranspiration and the salts of low solubility get precipitated. The salt to precipitate first is $CaCO_3$. Other salts like $CaSO_4$ and magnesium silicate also precipitate if the concentrations of these salts in soil solution exceed their solubility product constants (U. S. Salinity Laboratory Staff. 1954; Eaton *et al.*, 1968). This precipitation will decrease the soil salinity but concurrently increase the proportion of sodium in the soil solution and thus upset the dynamic equilibrium between the cations in solution and those adrorbed by the soil exchange complex. Under such conditions, a part of the originally adsorbed calcium and magnesium is replaced by sodium. The repetition of this process results in the formation of saline-sodic soils from saline soils. Therefore, it can be said that in arid regions such as Pakistan, saline soils provide the parent material for the development of sodic soils.

The Langlier index as modified by Bower (1961) is useful for knowing the expected precipitation of $CaCO_3$ from irrigation waters.

$$\text{Precipitation Index} = pH_s - pH_c \qquad 22$$

where, pH_s is the measured pH of saturated soil paste. It is generally equal to 8.4 for calcareous soils. pH_c is the calculated pH of the irrigation water in equilibrium with $CaCO_3$. A positive value of index indicates tendency of $CaCO_3$ to precipitate from irrigation water after its application to soil, while a negative value of index indicates tendency for $CaCO_3$ to be dissolved from soil. While taking care of concentration and precipitation factors, the following equation is obtained (Bower *et al.*, 1968) :

$$SAR_{ss} = SAR_{iw}\sqrt{C} + SAR_{iw}\sqrt{C}\,(pH_s - pH_c) \qquad 23$$

Taking pH of saturated paste of a calcareous soil as 8.4, the equation becomes :

$$SAR_{ss} = SAR_{iw}\sqrt{C} + SAR_{iw}\sqrt{C}\,(8.4 - pH_c) \qquad 24$$

$$SAR_{ss} = SAR_{iw}\sqrt{C}\,[1 + (8.4 - pH_c)] \qquad 25$$

The concentration of the soil solution will depend on the leaching fraction (LF). If only 10% of the irrigation water moves downward through the soil beyond the root zone, then LF = 0.1 and the concentration factor = 10. The above equation (No. 25) may also be written as :

$$SAR_{ss} = SAR_{iw}\sqrt{\frac{1}{LF}}\,[1 + (8.4 - pH_c)] \qquad 26$$

If the relationship between SAR and ESP is assumed to be one to one (this is approximately applicable up to ESP value of 50) then

$$ESP = SAR_{iw}\sqrt{\frac{1}{LF}}\,[1 + (8.4 - pH_c)] \qquad 27$$

The precipitation index is useful for classification of irrigation water and for predicting the expected SAR resulting from the use of a particular irrigation water. It will be clear from the following example of analysis of water from tubewell in Square No. 31, University of Agriculture, Faisalabad (Table 1). It was observed that after 4-5 irrigations with this water, the soil particles were dispersed because of increased exchangeable sodium and as a result of this the growth of citrus plants was adversely affected. Because of sodicity hazard the tubewell was dismantled. However, the analysis of this tubewell water does not indicate it to be so bad.

Table 1. *The sodium hazard (SAR) of tubewell irrigation water as indicated from its analysis and after applying the approach of Bower et al. (1969)*

	Milliequivalents per liter						
EC x 10^6	Ca + Mg	Na (by diff.)	CO_3	HCO_3	RSC	SAR	pH_c
			water analysis				
1200	3.19	8.81	0.59	7.43	4.83	7	7.2
			After 4 times concentration				
4800	12.76	35.24	2.36	29.72	—	14	—
		After precipitation of $CaCO_3$					
—	—	—	—	—	—	31*	—

*SAR calculated by using equation 25 and C = 4.

For estimating the sodicity hazard of irrigation waters in terms of the SAR of the surface soil (SARsu), Oster and Rhoades (1977) used the following equation:

$$SAR_{su} = SAR_{iw} \; 1 + 8.4 - pH_c \qquad 29$$

The SAR_{su} is numerically equal to SAR_{tdi} of irrigation water. Rhoapes (1968) applied the mineral weathering correction for estimating the sodicity hazard of irrigation waters at the lower boundary of the root zone (SAR_1) which leads to the equation ;

$$SAR_1 = \frac{Y^{(1 + 2\ LF)}}{\sqrt{LF}} \quad SAR_{1w}\ [1 + (8.4 - pH_c)] \qquad 29$$

where, 'Y' is the empirical mineral weathering parameter. The values of $\frac{Y^{(1 + 2\ LF)}}{\sqrt{LF}}$ are 2.06, 1.36, 1.03 and 0.83 at leaching fractions of 0.1, 0.2, 0.3 and 0.4, respectively where, Y and LF take on values between zero and one. These two equations are recommended for assessing the sodicity hazard of irrigation waters, because soil permeability and crop toxicity are distinctly sodium related hazards. With the use of these two equations, we can estimate the minimum (surface), maximum (bottom) and average profile SAR or ESP values resulting from the steady-state use of waters for irrigation.

The equation (29) along with three other equations was used for calculating the expected SAR (Table 2) at the bottom of the root zone ($SAR_{dw.}$) after growing three crops of sorghum, maize and sorghum. The SAR_{dw} values determined from the analysis of drainage water at steady state (Muhammed and Rauf, 1983) are also given in Table 2, while other 3 equations are given at the bottom of Table 2. Equation 30 gave the lowest, while equation 31 gave the highest values of SAR . Equation 32 gave slightly lower values than those of equation 31, while equation 29' which took into consideration the dissolution of salts from soil minerals (Rhoades, 1968) and precipitation of salts from irrigation water after application to soil (Bower, 1961), gave SAR_{dw} values almost equal to the observed ones. This clearly indicates that modification of the Gapon equation by various workers, leading to equation 29, is quite suitable for predicting the effects of a given water on the exchangeable sodium status of local soils. The values calculated by equation 29 gave a very high correlation coefficient ($r = 0.979$, $P = 0.01$) with observed values. The regression equation is :

$$Y = 1.93 + 1.014X$$

where, Y is the predicted SAR_{dw} and X is the calculated SAR_{dw} with equation 29. There is almost 1:1 relationship between observed and calculated values of SAR_{dw}. From this it is very clear that SAR_{dw} can be predicted very accurately by the equation of Rhoades (1968), which takes into consideration the dissolution of easily soluble minerals in soils developed under arid and semi-arid climate.

Table 2. *Observed and calculated steady-state SAR values of drainage waters as a function of LF*

Water No.	Observed	Calculated by equations 29	30	31	32	Observed	Calculated by equation 29	30	31	32
		...... LF = 0.051					...... LF = 0.103			
W_1	58.3	56.2	44.3	83.2	79.5	40.3	38.1	31.2	58.6	56.7
W_2	69.3	58.9	44.3	87.2	83.2	45.1	39.9	31.2	61.4	62.0
W_3	70.0	68.2	67.8	101.0	93.1	49.9	46.2	47.7	71.0	68.4
W_4	70.9	77.4	66.9	110.2	103.4	53.7	60.5	47.0	77.6	80.6
Ave.	64.6	64.4	56.8	95.4	89.8	47.2	43.7	39.3	67.8	67.1
		...... LF = 0.075					...... LF = 0.141			
W_5	60.9	57.2	37.6	86.2	84.7	40.0	39.8	27.4	62.8	59.2
W_6	58.7	58.9	36.2	85.8	79.2	38.5	39.6	26.4	62.6	56.8
W_7	72.2	70.0	54.8	105.5	106.6	52.6	48.7	39.9	77.0	72.3
W_8	79.0	74.1	55.1	111.7	104.3	56.7	51.6	40.2	81.5	74.1
Ave.	67.7	65.0	45.9	97.3	93.7	46.7	44.9	33.5	71.0	65.6
		...... LF = 0.099					...... LF = 0.188			
W_9	60.4	55.4	32.7	85.5	84.6	43.2	38.0	23.8	62.0	60.1
W_{10}	62.6	55.4	31.8	84.8	82.4	40.0	37.7	23.1	61.6	57.8
W_{11}	71.8	69.9	47.4	107.1	103.6	46.8	47.6	34.4	77.7	72.0
W_{12}	79.9	72.6	48.0	111.2	110.7	49.8	49.4	34.8	80.7	75.2
Ave.	68.7	63.4	40.0	97.2	95.3	45.0	43.2	29.0	70.5	66.3

$$SAR_{dw} = \frac{1}{\sqrt{LF}} = SAR_{iw} \qquad (30)$$

$$SAR_{dw} = \frac{1}{\sqrt{LF}} = SAR_{iw}\ [1 + (8.0 - pH_c)] \qquad (31)$$

$$SAR_{dw} = \frac{1}{\sqrt{LF}} = SAR_{iw}\ [1 + (8.0 - pH_c)] \text{ where } LF = \frac{Cl_{iw}}{Cl_{dw}} \quad (32$$

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