Calculating Cation Exchange in a Salt Transport Model[1]

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ABSTRACT

A cation exchange subroutine that can be expanded to include any number of cations was developed and interfaced with a water flow-salt transport model that also contained a lime and gypsum precipitation-dissolution chemistry subroutine. The exchange subroutine was required by the complete model to satisfactorily predict EC, SAR, and specific ion concentration changes with time and depth for a gypsiferous and a non-gypsiferous soil irrigated with waters containing three different $CaSO_4$ concentrations at two leaching fractions. In his sudy, exchangeable Ca, Mg, Na, and K were considered. Exchangeable K was included for use with high exchangeable and soluble K soils and high K irrigation waters. The additional cation exchange coefficient values needed for K exchange and a method for their calculation is given.

Additional Index Words: exchangeable cations, sodium adsorption ratio (SAR), cation exchange capacity (CEC).

CATION EXCHANGE MODELS, used in salt transport simulations have traditionally considered only Ca-Mg-Na exchange reactions (Dutt et al., 1972; Jury et al., 1978; Paul et al., 1966) and Ca and Mg have often been combined and considered as a single species (U.S. Salinity Laboratory Staff, 1954). Agricultural processing wastewaters, that apply from 600 to 7,700 kg K/ha each year, are being used for irrigation (Smith et al., 1978) and saline and saline-sodic soils are being reclaimed that contain from 30 to 80 meq/liter K in the saturation extracts. As high as 85% of the exchangeable cations in these soils are K (author's unpublished data). Salt transport and storage in these soils and soils being irrigated with high K waters cannot be adequately simulated unless K exchange and transport are considered.

This paper describes the background and development of a mechanistic cation exchange model that includes K exchange. This model was interfaced as a subroutine with a water movement-salt transport model designed to describe salt transport and storage in calcareous soils with and without gypsum, irrigated with waters containing three different $CaCO_4$ concentrations. (Robbins et al., 1980).

Cation exchange reactions can be described by one of two conventions. The Vanselow convention designates the anion exchange charge as −1 and the reacting cations are designed in molar quantities. The exchange reaction is represented as:

$$nMX_m + mN^{n+} = nM^{m+} + mNX_n \qquad [1]$$

where M and N are metal cations with charges of m^+ and n^+, respectively. The Gapon convention represents the cations reacting as equivalents and takes the form

$$nmM_{1/m}X + mN^{n+} = nM^{m+} + mnN_{1/n}X.$$
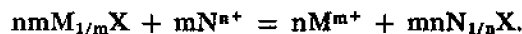
These two conventions are compared and explained in detail by Sposito (1977). By dividing both sides of Eq. [1] by nm, and by using a slightly different notation, the equation becomes

$$X_{1/mM} + 1/nN^{n+} = X_{1/nN} + 1/mM^{m+} \qquad [2]$$

still maintaining a −1 charge on X. It should be recognized that on a molecular scale $1/mM^{m+}$ or $1/nN^{n+}$ (for m > 1 and n > 1) does not exist, however, on a macroscale this form is thermodynamically equivalent and better lends itself to modeling multication systems.

Equation [2] can be evaluated as the equilibrium relationship

$$K = \frac{X_{1/nN} \ (M^{m+})^{1/m}}{X_{1/mM} \ (N^{n+})^{1/n}} \qquad [3]$$

where K is the selectivity coefficient.

Dutt et al. (1972) substituted exchange cations similar to Eq. [3] for Ca-Mg and Ca-Na equilibrium, expressed in terms of X_{Mg} and X_{Na}, into the equation

$$CEC = X_{Na} + X_{Mg} + X_{Ca}$$

and then by rearranging they obtained the expression

$$X_{Ca} = CEC \div \left[\frac{(Mg) \ K_1}{(Ca)} + \frac{(Ca)^{\frac{1}{2}} \ K_2}{(Na)} + 1 \right]$$

where K_1 and K_2 are the selectivity coefficients for the Ca-Mg and Na-Ca exchange relationships, respectively, and CEC is the cation exchange capacity. The terms (Na), (Ca), and (Mg) represent sodium, calcium, and magnesium activities in solution.

Values for X_{Na} were then calculated using Eq. [3] for (Na) and (Ca). Exchangeable Mg was then calculated as the difference between the CEC and exchangeable Ca plus Na. Potassium was considered insignificant in their model.

In attempting to obtain selectivity coefficients that are valid for all salt mixtures and exchange materials, a number of workers have shown increased agreement between selectivity coefficient values calculated for a given system with varying anion ratios and concentrations, when ionic strength and ion pair corrections were made for solution cation activities (Babcock and Schulz, 1963; Dutt and Doneen, 1963; Rao et al. (1968); and Van Beek and Bolt, 1973). In order to use cation activities in the above type of calculations, the soil solution must be considered a "true solution" in the sense that cation activities are not affected by presence of soil minerals. Dutt and Anderson (1964) suggested that this is the case with respect to gypsum solubility, however, this may not be the case near charged surfaces.

For some cation exchange reactions, particularly K and NH_4, a hysteresis effect has been reported (Bar-

shad, 1954) and the selectivity coefficient values depended on whether they were calculated from adsorption or desorption cycles.

THEORY

The XCHANG subroutine as developed for this study uses the notation as developed in Eq. [3], and assumes that the CEC is a constant for a given soil, independent of pH, ion type and concentration, that the soil solution is a "true solution", in that cation activities are not affected by the presence of charged surfaces and that cation exchange is a reversible process. The subroutine does not consider anion exchange and further assumes that the sum of exchangeable cations are equal to the CEC. That is

$$CEC = X_{\frac{1}{2}Ca} + X_{\frac{1}{2}Mg} + X_{Na} + X_K \qquad [4]$$

where $X_{\frac{1}{2}Ca}$, $X_{\frac{1}{2}Mg}$, X_{Na}, and X_K are the exchangeable cations (meq/100 g).

The selectivity coefficients K_1 through K_6 for the equilibrium between the cations in solution and the exchangeable cations are defined as:

$$\frac{(Ca)^{\frac{1}{2}}}{(Mg)^{\frac{1}{2}}} \frac{X_{\frac{1}{2}Mg}}{X_{\frac{1}{2}Ca}} = K_1 \quad [5] \qquad \frac{(K)}{(Mg)^{\frac{1}{2}}} \frac{X_{\frac{1}{2}Mg}}{X_K} = K_4 \qquad [8]$$

$$\frac{(Na)}{(Ca)^{\frac{1}{2}}} \frac{X_{\frac{1}{2}Ca}}{X_{Na}} = K_2 \quad [6] \qquad \frac{(Na)}{(Mg)^{\frac{1}{2}}} \frac{X_{\frac{1}{2}Mg}}{X_{Na}} = K_5 \qquad [9]$$

$$\frac{(K)}{(Ca)^{\frac{1}{2}}} \frac{X_{\frac{1}{2}Ca}}{X_K} = K_3 \quad [7] \qquad \frac{(Na)}{(K)} \frac{X_K}{X_{Na}} = K_6 \qquad [10]$$

Cation activities used in the above equations are corrected for ionic strength effect and ion pairing in the chemistry subroutine (Robbins et al., 1980).

The equation for calculating $X_{\frac{1}{2}Ca}$ is developed by rewriting Eq. [5], [6], and [7] in terms of $X_{\frac{1}{2}Mg}$, X_{Na}, and X_K, and substituting them into Eq. [4]. $X_{\frac{1}{2}Ca}$ is factored from each right hand term and the resulting equation is then rearranged to give

$$X_{\frac{1}{2}Ca} = CEC \div \left[\frac{(Mg)^{\frac{1}{2}} K_1}{(Ca)^{\frac{1}{2}}} + \frac{(Na)}{(Ca)^{\frac{1}{2}} K_2} + \frac{(K)}{(Ca)^{\frac{1}{2}} K_3} + 1 \right].$$

Following this same procedure for Mg, Na, and K gave equivalent equations for calculating $X_{\frac{1}{2}Mg}$, X_{Na}, and X_K.

The resulting four equations are the basis of the cation exchange subroutine which equilibrates solution activities with exchangeable cation concentrations during salt precipitation or dissolution. Initial exchangeable cation concentration are calculated from the soil CEC, the solution cation activities, and the selectivity coefficients for the appropriate exchange reac-

tions. In subsequent exchangeable cation-solution cation adjustments, the solution cation concentration, volumetric water content, and bulk density are also needed for each soil depth increment.

In principle the above approach can be expanded to any number of cations, provided the selectivity coefficients can be approximated for all possible cation pair exchange reactions.

METHODS

Computer model validation and selectivity coefficient calculation data were obtained from a lysimeter study described elsewhere (Robbins, 1979;[3] Robbins et al., 1980). X-ray diffraction data for the two soils used showed only illite and kaolinite type clay minerals in about equal quanties.

One sample of each soil was taken at the beginning and seven samples of each were taken at the end of the study. The samples were selected to give as wide an exchangeable cation ratio range as possible under the study conditions. Saturation extract electrical conductivity (EC) and Ca, Mg, Na, K, Cl, SO₄, and HCO₃ concentrations were determined for each soil sample (Table 1). Ammonium acetate extractable Mg, Na, and K, and CEC were also determined in duplicate on each sample. Exchangeable Mg, Na, and K were calculated as the difference between the saturation and the ammonium acetate extractable values. Since both soils contain lime and gypsum, exchangeable Ca was calculated as the CEC minus the three measured exchangeable cations. Ionic strength was calculated from the measured EC (Griffin and Jurinak, 1973) and activity coefficients were calculated by the Davies equation (Stumm and Morgan, 1970). After correcting for the ion pairs CaCO₃⁰, CaSO₄⁰, CaOH⁺, CaHCO₃⁺, MgCO₃⁰, MgSO₄⁰, MgOH⁺, MgHCO₃⁺, NaSO₄⁻, and NaCO₃⁻, activities were calculated for the four exchangeable cations in each soil sample extract (Table 2). Using the measured exchangeable cation values, calculated cation activities, and Eq. [3] through [8], selectivity coefficients for each ion pair in each sample were calculated (Table 2). Only K_3 was significantly different for the two soils.

The values obtained for K_1, K_2, and K_3 are compared with values found in the literature for other soils and clays (Table 3). The values reported for K_1 were generally between 0.5 and 1.1 for soils and clays with the exception of two tropical soils and peat. All K_2 values listed were between 5.6 and 7.1. The K_3 values obtained by Udo (1978) for a kaolinite clay at 30°C were similar to the values from these soils except when the X_K was 0.1 of the CEC.

The soil solution ion concentrations and the EC and SAR values predicted by the complete model were compared with values measured in samples extracted from two different soils irrigated with water containing three CaSO₄ concentrations at

[3] C. W. Robbins. 1979. A salt transport and storage model for calcareous soils that may contain gypsum. Ph.D. Diss. Utah State Univ., Logan, Utah.

Table 1—Saturation extract data used to calculate the selectivity coefficients for the XCHANG subroutine.

Sample	Solution ion concentrations							EC	Exchangeable ions			
	Ca	Mg	Na	K	Cl	SO₄	HCO₃		X_{Ca}	X_{Mg}	X_{Na}	X_K
			meq/liter					mmho/cm		meq/100 g		
Penoyer loam												
1	33.40	9.70	1.23	3.71	1.70	39.50	5.80	3.0	4.46	1.87	0.01	0.56
2	24.50	17.33	35.05	3.33	42.40	36.05	1.90	5.6	3.78	2.37	0.29	0.46
3	25.35	17.67	33.33	3.67	53.80	27.50	1.90	6.2	3.89	2.23	0.26	0.52
4	17.10	11.10	14.33	4.00	14.90	30.80	1.60	3.4	4.17	2.01	0.12	0.60
5	30.01	34.08	5.67	3.67	34.80	30.60	2.50	5.7	3.46	2.93	0.04	0.47
6	11.20	4.87	7.72	1.67	1.60	21.00	1.80	1.8	4.55	1.81	0.11	0.43
7	16.30	10.00	5.67	4.33	3.90	31.20	1.70	2.7	4.00	2.12	0.05	0.73
8	15.00	11.67	16.84	3.53	4.20	45.10	2.70	3.2	3.53	2.41	0.19	0.77
Hunting silty clay loam												
9	18.00	8.96	6.04	1.67	8.21	17.30	8.90	2.7	10.16	4.02	0.13	0.59
10	56.35	25.62	15.21	2.08	17.47	70.50	8.10	7.5	9.89	4.24	0.23	0.54
11	38.25	19.37	17.92	2.71	39.70	31.10	7.70	7.0	9.41	4.41	0.32	0.76
12	52.31	26.46	23.21	2.92	69.08	27.60	8.10	9.5	9.67	4.25	0.30	0.66
13	34.31	18.75	8.33	3.33	16.88	38.60	7.40	6.0	9.45	4.43	0.15	0.87
14	38.25	15.21	5.00	2.08	2.25	49.40	8.00	4.5	10.63	3.56	0.10	0.61
15	42.75	20.41	26.87	1.84	40.85	41.40	8.10	7.5	10.01	3.95	0.41	0.53
16	28.13	12.06	11.87	1.87	10.92	35.50	7.90	4.4	10.05	3.87	0.28	0.70

Table 2—Cation activities and selectivity coefficients calculated from data in Table 1.

Sample	Treatment	Sample depth	Cation activities				K_1	K_2	K_3	K_4	K_5	K_6
			Ca	Mg	Na	K						
		cm	mmol/liter									
				Penoyer loam								
1			5.0	1.6	1.0	3.1	0.74	6.3	0.35	0.26	4.7	18.1
2	5	0–12	3.5	2.7	27.6	2.7	0.73	6.1	0.38	0.27	4.4	16.2
3	5	12–25	3.9	2.9	26.2	2.9	0.66	6.3	0.35	0.23	4.2	18.1
4	5	25–50	2.7	1.9	11.6	3.3	0.58	7.8	0.44	0.25	4.5	17.6
5	13†	0–25	4.7	5.6	4.5	2.9	0.78	5.7	0.31	0.24	4.4	18.2
6	14	12–37	2.0	0.9	6.6	1.4	0.59	6.1	0.33	0.20	3.6	18.4
7	14	37–62	2.6	1.7	4.5	3.6	0.66	7.1	0.39	0.25	4.6	18.3
8	14	62–87	2.0	1.7	13.6	2.9	0.74	5.6	0.30	0.22	4.2	19.0
		Selectivity coefficient means and standard deviations					0.69 ±0.07	6.4 ±0.7	0.36 ±0.04	0.24 ±0.02	4.3 ±0.3	18.0 ±0.8
				Hunting silty clay loam								
9			3.4	1.6	5.0	1.4	0.54	6.7	0.41	0.22	3.6	16.2
10	7	10–25	6.5	3.2	11.5	1.6	0.61	6.1	0.36	0.22	3.7	16.8
11	9	0–10	5.7	3.0	13.9	2.1	0.55	5.4	0.34	0.22	3.5	15.7
12	9	10–25	7.5	3.9	17.7	2.3	0.61	6.6	0.38	0.23	4.0	17.4
13	9	25–50	4.8	2.8	6.5	2.7	0.61	5.9	0.42	0.26	3.6	14.0
14	10	0–15	5.2	2.2	4.0	1.7	0.51	5.8	0.41	0.21	3.0	14.4
15	11	0–25	5.8	2.9	20.7	1.4	0.56	6.6	0.35	0.19	3.7	19.1
16	11	37–62	4.2	1.9	9.6	1.5	0.57	5.3	0.33	0.19	3.0	16.0
		Selectivity coefficient means and standard deviations					0.58 ±0.05	6.1 ±0.5	0.37 ±0.04	0.22 ±0.02	3.5 ±0.3	16.2 ±0.6

† The alfalfa plants were removed after the main lysimeter study was completed and treatment 4 was leached four times with 35 mm of distilled water and treatment 1 was leached four times with 35 mm of 40 meq/liter $MgCl_2$ solution. These were designated as treatment 13 and 14, respectively. The lysimeters were covered to retard surface evaporation during these leachings.

two different leaching fractions. The soil solution samples were obtained from ceramic cups in the sides of the lysimeters at depths of 0.25, 0.50, and 0.75 m from the soil surface (Robbins and Willardson, 1980). The chemistry subroutine results are described elsewhere (Robbins et al., 1980).

The combined transport-chemistry-exchange model was designed with three calculation method options. Salt could be moved through the soil profile (i) without chemical reaction with the soil (SALTFLOWI), (ii) in combination with chemical

precipitation and dissolution (SALTFLOWII), or (iii) with chemical precipitation and dissolution combined with cation exchange equilibrium reactions (SALTFLOWIII). These options were provided to determine the influence of the two subroutines on the values predicted for salt exchange, storage, and flow.

RESULTS

In all 12 treatments, SALTFLOWIII gave the best prediction of all measured parameters, however, in some cases one of the other calculation options also gave satisfactory predictions for a particular parameter. Only treatment 6 and 7 of the 12 treatments modeled will be discussed in detail. Treatment 6 was the irrigation of Penoyer loam with water containing 5.0 meq/liter Ca and 0.5 meq/liter SO_4 at a 25% leaching fraction. This soil initially contained 0.7% gypsum by weight and this treatment produced the greatest gypsum dissolution rate of those used in this study. Treatment 7 consisted of irrigating Hunting silty clay loam with water containing 12 meq/liter Ca and 12 meq/liter SO_4 at a 10% leaching fraction. This soil initially did not contain gypsum, but of the treatments applied to this soil, this treatment produced the greatest amount of gypsum precipitation. The Penoyer loam has a CEC of 6.9 meq/100 g and Hunting silty clay loam has a CEC of 14.9 meq/100 g.

Predicted exchangeable Na, K, Mg, and Ca values are shown together with the original measured values in the Penoyer soil (Fig. 1) and the Hunting soil (Fig. 2). In both cases the predicted exchangeable Ca increased in the upper depth increments and decreased lower in the profile. This was balanced by exchangeable Mg, and K decreases in the upper profile and increases in the lower part of the profile. Exchangeable Na increased throughout the profile in treatment 6. In treatment 7, Na was desorbed in the surface and adsorbed in the lower depths. It should be noted

Table 3—Selectivity coefficient values used for this study compared with values found in the literature.

	K_1 (Ca-Mg)	K_2 (Na-Ca)	K_3 (K-Ca)
This study			
Penoyer loam (coarse-silty, mixed (calcareous) mesic Typic Torriorthents]	0.69	6.4	0.36
Hunting silty clay loam [fine-silty, mixed (calcareous), mesic Aquic Ustifluvents]	0.58	6.1	0.37
Clark (1966)			
Wyoming bentonite	1.06		
Hunsaker and Pratt (1971)			
Brazilian loam	6.52		
Aiken soils	5.46		
Krishnamoorthy and Overstreet (1950)			
Utah bentonite	0.92		
Yolo clay	0.70		
Paul et al. (1966)			
Oakley soil	0.64	5.5	
Hanford soil	0.54	7.0	
Arbuckle soil	0.59	5.6	
Yolo soil	0.67	7.1	
Sacramento soil	0.66	5.8	
Salmon (1964)			
Wyoming bentonite	0.82		
Blisworth illite	0.82		
Peat	0.20		
Udo (1978)			
Kaolinite (30°C) X_R			
0.1	0.68		0.03
0.2	0.64		0.27
0.3	0.64		0.29

* X_R is the ratio of the exchangeable cation to CEC at which these values were measured.
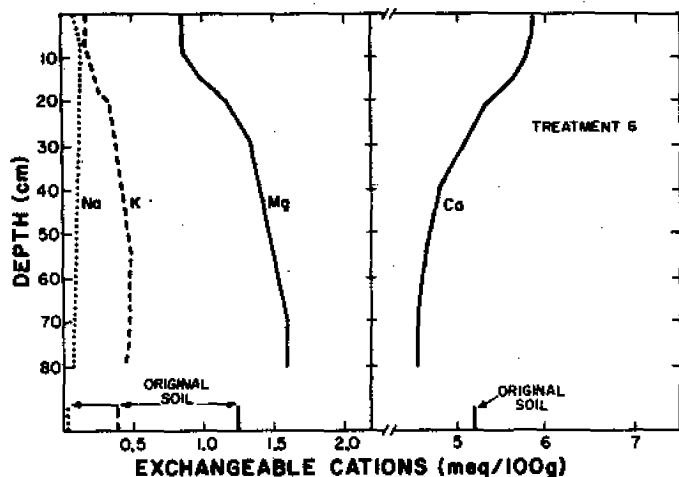
Fig. 1—Calculated exchangeable Na, K, Mg, and Ca concentration for treatment 6 after 248 days and the measured exchangeable cations in the Penoyer soil as it was added to the lysimeters.

Fig. 2—Calculated exchangeable Na, K, Mg, and Ca concentrations for treatment 7 after 248 days and the measured exchangeable cations in the Hunting soil as it was added to the lysimeters.

that for Penoyer soil (CEC = 6.9 meq/100 g), the boundary between desorption and adsorption of Ca is not as abrupt as that for the Hunting soil (CEC = 14.9 meq/100 g). This is considered to be due to the difference in CEC values for the two soils.

Satisfactory SAR and EC prediction for any treatment was only possible with SALTFLOWIII after the lysimeters had been operated for 190 days. Electrical conductivity predictions are discussed elsewhere (Robbins et al., 1980).

Predicted SAR values by SALTFLOWI were too high at the 25 and 50 cm depths after 248 days for treatment 6. SALTFLOWII also predicted high values at 50 and 75 cm on day 248. This trend was observed for all treatments when gypsum was being dissolved from the soil profile. By day 248 the SALTFLOWI calculation underestimated SAR at the 25 and 50 cm depths while SALTFLOWII overestimated the SAR for those depths for treatment 7. This trend was observed for those treatments where gypsum was being precipitated from soil solution (Fig. 3). This agrees with the conclusion of Jury et al. (1978), that with-
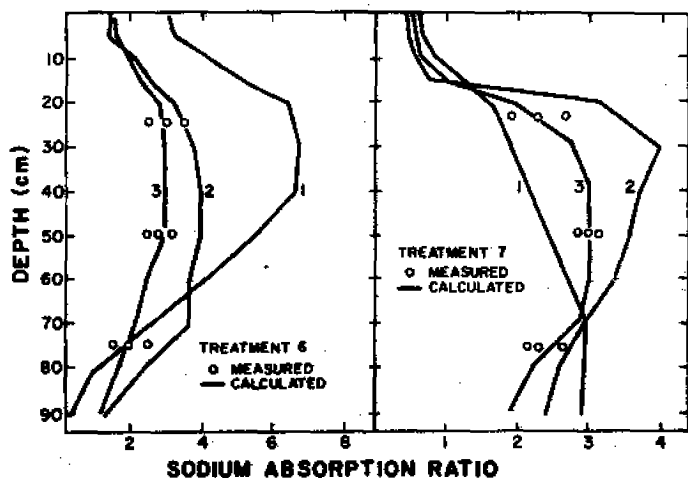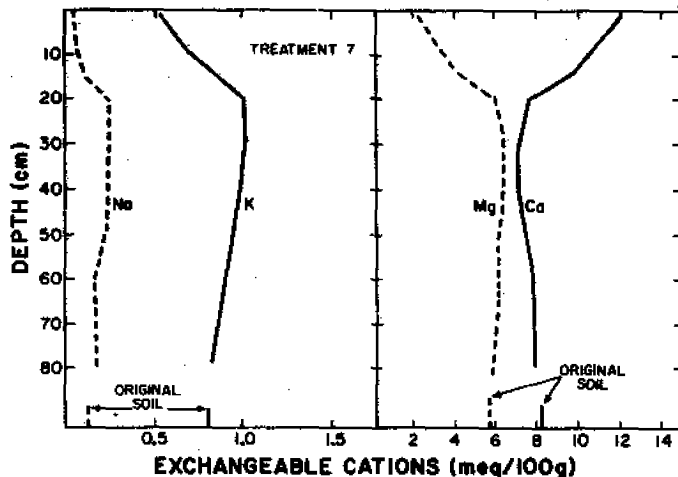
out considering exchange, EC and SAR could not be predicted when the irrigation water was near lime or gypsum saturation or when irrigation managements significantly altered the soil solution salt composition because of the EC-SAR-ESP-gypsum solubility interactions.

To explain the differences in the ability of the three options to predict EC and SAR, it is necessary to look at individual ion prediction since they are each handled slightly differently by the three models due to the differences in chemical behavior.

Cloride ion was considered to move independently of chemical reactions and cation exchange and was satisfactorily predicted for all treatments by all three calculation options when the calculated water movement into and out of the soil profiles corresponded to the measured water movement into and out of the lysimeters (Robbins et al., 1980). This would suggest that the basic salt transport and water flow model was working properly. The solute transport and water

Fig. 3—Measured SAR values and values calculated by (1) SALTFLOWI, (2) SALTFLOWII, and (3) SALTFLOWIII for treatments 6 and 7 on day 248.
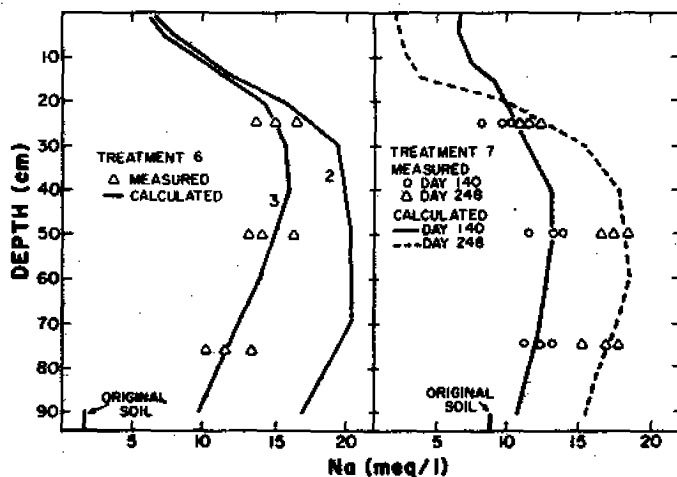

Fig. 4—Measured Na concentrations and concentrations calculated by (2) SALTFLOWII, and (3) SALTFLOWIII for treatment 6 on day 248 and measured and calculated (SALTFLOWIII) Na concentrations for treatment 7 on day 140 and 248.

flow model of Childs and Hanks (1975) was assumed to have been validated by them and others who have used it and no attempt was made to revalidate it.

Sodium concentration in soil solution was satisfactorily predicted only by SALTFLOWIII (Fig. 4). In treatment 6, the soil originally contained 1.5 meq Na/liter in the saturation extract and was irrigated with water containing 6 meq Na/liter. Some of the Na applied was exchanged for other ions. This explains part of the overestimation of SAR by SALT-FLOWII (Fig. 3). At the same time Ca was leached from the surface of the gypsiferous soil when irrigated with a low SO_4 water, thus when dissolution of gypsum was not considered in this and other treatments, SAR predictions were higher than when SALTFLOWIII was used (Robbins et al., 1980). When chemical precipitation was not considered in treatment 7, Ca concentration predictions were extremely high and consequently the SAR predictions were low. This explains in part the SAR underestimation for treatments where gypsum was precipitating when only salt transport (SALTFLOWI) was simulated. In treatment 7 the Na concentration decreased in the surface and increased below 25 cm with time (Fig. 4). This was simulated only by SALTFLOWIII.

Estimations of K and Mg concentrations were also satisfactory for all treatments when SALTFLOWIII was used (Fig. 5). When cation exchange was not considered, the predicted movement of these cations from the upper soil depth increments was too rapid because the irrigation waters for treatment 6 (0.5 meq/liter K and 1.0 meq/liter Mg) and 7 (0.5 meq/liter K and 3.5 meq/liter Mg) contained a significantly higher ratio of Ca to K and Mg than did the soil solutions (Robbins et al., 1980).

CONCLUSIONS

Interfacing a chemical precipitation–dissolution subroutine and a cation exchange subroutine with an existing water movement–salt transport model provided a computer program that satisfactorily predicted EC, SAR, and Ca, Mg, Na, K, Cl, HCO_3, and SO_4 concentrations in the soil solution for the 12 treatments studied. The chemistry subroutine was necessary for Ca, SO_4, HCO_3, and CO_3 predictions when precipita-

tion or dissolution of lime and gypsum were involved. The cation exchange subroutine was required for satisfactory Ca, Mg, Na, K, and SO_4 predictions when the cation ratios in the irrigation water differed from those of the soil solution. Both subroutines were required for reasonable EC and SAR calculation.

The model needs to be tested under conditions of reclaiming and development of saline-sodic and sodic soils and also needs to be tested for soils receiving high salt concentration waters (brines) to determine the upper limit of its applicability for extremely saline conditions. Obtaining selectivity coefficients for a variety of soils by the method used here needs further consideration. Selectivity coefficients for adsorption as well as desorption for each cation used also need to be evaluated to determine the possibility of hysteresis effects and their consequences. The exchangeable cation values predicted by SALTFLOWIII agreed satisfactorily with the limited number of samples taken at the end of the study. The cation exchange subroutine was also indirectly validated, in that, without it the predicted and measured soil solution values did not agree. The cation exchange model does, however, need further direct validation by comparing measured and predicted exchangeable cation values.

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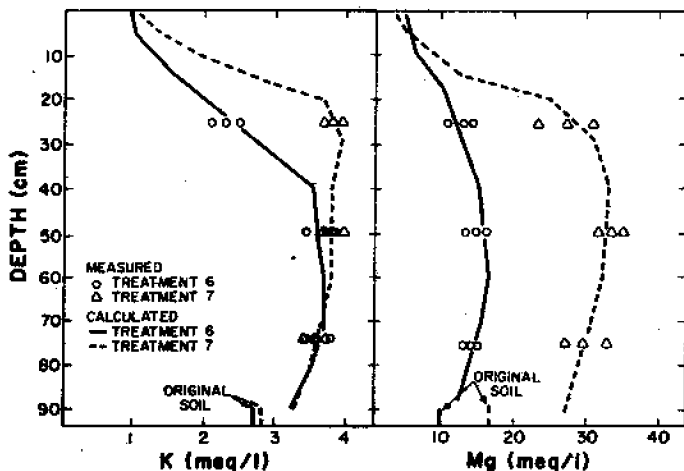16. Salmon, R. C. 1964. Cation exchange reactions. J. Soil Sci. 15:273–283.

Fig. 5—Measured and calculated (SALTFLOWIII) K and Mg concentrations for treatments 6 and 7 on day 248.

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