

# SODIC SOIL RECLAMATION USING MULTICOMPONENT TRANSPORT MODELING

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By Jiří Šimůnek<sup>1</sup> and Donald L. Suarez<sup>2</sup>

**ABSTRACT:** High contents of soluble salts accumulated in a soil can significantly decrease the value and productivity of agricultural lands. Present recommendations for reclamation are usually based only on relatively simple and often empirical relations. In this paper we give a brief overview of many unique physical and chemical factors important to reclamation contained in the one-dimensional multicomponent transport model UNSATCHEM and demonstrate its use for evaluating the reclamation of a sodic soil using various amendments and management strategies. We evaluate particular reclamation strategies based on the following considerations: (1) the quantity of water needed; (2) the quantity of amendments to be used; and (3) the time required for reclamation to be completed. Our study concentrates primarily on such chemical reactions as cation exchange, precipitation, and dissolution of solid phases (reclamation amendments) and on the effect of solution composition on the soil hydraulic properties and corresponding changes in the water flow and solute transport rates.

## INTRODUCTION

Agricultural productivity in many areas of the world is adversely affected by excess soil salinity. It is estimated that about 25% of all the irrigated land is salt affected (Suarez and Rhoades 1991) to the extent that its agricultural productivity is either mildly or severely affected. The adverse impact of salinity and sodicity problems is particularly acute in arid and semiarid regions of the world that require increased food production to keep up with rapid population growth. Urbanization is a problem in most or all countries resulting in farmers cultivating land that is less suitable for agricultural purposes and often under conditions of elevated salinity or sodicity. Urbanization also results in increased demands for high-quality water. Hence, farmers will be increasingly required to use alternative water supplies for irrigation, including urban waste waters that are elevated in Na. Use of marginal waters for irrigation, as well as requirements for the more efficient use of available water, will increase demands for reclamation to improve the physical and chemical properties of soils. High costs associated with Ca amendments and the time and expense needed for leaching with suitable water makes it important to optimize reclamation practices.

High content of soluble salts accumulated in the soil can significantly decrease the agricultural productivity by imposing osmotic stress on growing crops, resulting in decreased crop yields and possibly even crop failure. Moreover, accumulation of monovalent cations, particularly Na, may lead to clay dispersion, swelling, and overall poor soil physical properties. These processes have an adverse effect on the water transmission properties of a soil, including hydraulic conductivity, infiltration rates, soil water retention (Shainberg and Levy 1992), and soil tilth. These negative effects are usually explained on the basis of the diffuse double layer theory. Monovalent cations satisfy the negative charge of clays at a greater distance away from the surface than divalent cations, thus leading to a more extensive diffuse double layer for monovalent cations. The same is true for a dilute as compared to a

high-electrolyte soil solution. A consequence of the more diffuse double layer associated with monovalent ions is the greater repulsion force or swelling pressure between neighboring clay platelets, a situation that results in swelling and also dispersion. In addition, Suarez et al. (1984) determined that elevated levels of pH also can have an adverse effect on hydraulic conductivity in experiments in which the pH effects were compared at otherwise constant exchangeable Na and salinity levels.

Reclamation of sodic soils has been recommended to reduce the exchangeable sodium percentage to below 15, a historical criterion for distinguishing between sodic and nonsodic conditions ("Diagnosis" 1954; Bresler et al. 1982). The processes of soil dispersion, swelling, and loss of aggregate stability that often accompany higher values of exchangeable sodium depend also on many other factors such as soil mineralogy, salinity, pH, soil texture, organic matter, and management practices. Much of the early work concerning reclamation of sodic soils was of a trial and error nature because of a lack of understanding of the underlying processes. Even current recommendations for reclamation are mostly based on simple empirical relations involving the sodium adsorption ratio (SAR) or exchangeable sodium percentage (ESP) and salinity [e.g., Rhoades (1968)], as well as corrections of SAR to account for CaCO<sub>3</sub> (Suarez 1981) or gypsum dissolution [e.g., Hira et al. (1981), Rhoades (1982)].

Recommended quantities of amendments and water needed for reclamation are generally based on implicit assumptions regarding ion exchange selectivity and leaching efficiency. Efficient reclamation of sodic soils includes minimizing the quantity of amendments required for adequate water infiltration. Adding excess amendments because of inaccurate assumptions involved in reclamation calculations results in additional time, extra expense, and increased salt loading to the ground water. Traditional recommendations [e.g., "Diagnosis" 1954] include reclamation based on the calculation of the mol. of Na to be exchanged so as to reduce ESP below a desired level. Exchange reactions do not go to completion (as there is an equilibrium between Na and Ca), causing some Ca to be lost from the reclamation zone during leaching. Hence, recommendations exist to apply a quantity of Ca equal to 1.25 times the amount of Na to be exchanged to compensate for the incomplete exchange ("Diagnosis" 1954). The degree of exchange efficiency depends on many factors, including the assumption of exchange equilibrium, Ca-Na exchange selectivity, the concentration of Ca being released by the amendment, the total salt concentration, and the existing ESP. Accurate determination of amendment and water requirements requires a model that quantitatively addresses and integrates all of these factors.

<sup>1</sup>Asst. Res., U.S. Salinity Lab., U.S. Dept. of Agr., Agric. Res. Service, 450 W. Big Springs Rd., Riverside, CA 92507.

<sup>2</sup>Res. Leader, U.S. Salinity Lab., U.S. Dept. of Agr., Agric. Res. Service, 450 W. Big Springs Rd., Riverside, CA.

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Initial attempts to describe and quantify the reclamation processes were based mostly on chromatographic models (Dutt et al. 1972; Tanji et al. 1972). Models of this type assume that the soil profile is stratified chemically and physically into a series of horizontal layers (or "plates"), with water moving from one layer to another by piston flow. Chemical processes between the solution, exchanger, and soil mineral phase within a particular plate were assumed to be instantaneous equilibrium processes. The models by Dutt et al. (1972) and Tanji et al. (1972) both considered major ion species, several complexation reactions, cation exchange, and mineral dissolution of gypsum and calcite. Since these two models do not consider explicitly the soil hydraulic conductivity and water flow velocities, they cannot predict if the amendment is concentrated enough to significantly improve the infiltration rate. Hence, they cannot accurately predict the time required to complete the reclamation process. Nevertheless, both models provided powerful tools for quantitative predictions of the water and amendment required to reclaim soil profiles to desired levels of salinity and ESP.

More efficient use of amendments and improved management of the reclamation process based on mathematical calculations requires consideration of other relevant processes. For example, knowledge is required of the soils' hydraulic properties, including their response to changes in the chemical composition of the soil water. This is because the solution chemistry can have a significant effect, especially on the soil hydraulic conductivity. The soil hydraulic conductivity can be reduced by several orders of magnitude, while the effect on water content is much smaller (Russo 1988). Models that describe the effects of sodicity and salinity on hydraulic conductivity can be divided into two broad groups: theoretical models based on double-layer theory (Lagerwerff et al. 1969; Russo and Bresler 1977; Russo 1988) and semiempirical models (Yaron and Thomas 1968; McNeal 1968, 1974). McNeal's model is based on a simple clay-swelling model, where clay swelling is related to decreases in soil hydraulic conductivity.

The complex chemical processes involved in the reclamation of sodic soils include precipitation and/or dissolution of solid phases, cation exchange (mostly involving Na, Ca, and K), and complexation reactions, in addition to variably saturated water and solute flow. Therefore, accurate simulation of sodic soil reclamation requires application of multicomponent transport models that consider variable saturated water flow. Only recently has there been a significant effort to develop multicomponent transport models that can handle all of the pertinent chemical processes. Recent reviews on the development of general hydrogeochemical transport models of reactive multicomponent components are given by Yeh and Tripathi (1989) and Mangold and Tsang (1991). Most multicomponent transport models were developed for saturated ground-water flow. Coupling of equilibrium chemistry submodels to numerical variably saturated water flow and solute transport models has been limited (Robbins et al. 1980; Russo 1986; Wagenet and Hutson 1987; Šimůnek and Suarez 1994; Suarez and Šimůnek, unpublished paper, 1997). Also, none of the reclamation models developed so far consider dynamic changes in CO<sub>2</sub> concentrations that can significantly affect pH and the solubility of calcium carbonate. Finally, known kinetic features of dissolution and precipitation processes for calcite and dissolution of dolomite may need to be considered. These are all unique features of the UNSATCHEM model (Šimůnek et al. 1996).

In this paper we give a brief overview of the one-dimensional multicomponent transport model UNSATCHEM and demonstrate its use for evaluating the reclamation of a sodic soil using various amendments and management strategies. We evaluate particular reclamation strategies based on the follow-

ing important considerations: (1) the quantity of water needed; (2) the quantity of amendments to be used; and (3) the time required for reclamation to be completed. In our analysis we will concentrate on cation exchange, precipitation, and dissolution of solid phases (reclamation amendments), as well as the effects of solution composition on the soil hydraulic properties and corresponding changes in water flow and solute transport rates.

## MODEL DEVELOPMENT

### Conceptual Description

The one-dimensional UNSATCHEM model (Šimůnek et al. 1996; Suarez and Šimůnek, unpublished paper, 1997) consists of an unsaturated water flow model coupled to a multicomponent solute transport module. The model has submodels accounting for major ion chemistry, multiphase gas transport, CO<sub>2</sub> production/transport, and heat transport (Šimůnek and Suarez 1993, 1994). Soil temperature is required for predicting CO<sub>2</sub> production and for evaluating thermodynamic equilibrium and kinetic rate constants. The concentration of CO<sub>2</sub> in the soil profile is a dynamic variable needed for predicting the pH (and thus the hydraulic properties), as well as the soil solution composition.

### Variably Saturated Water Flow

One-dimensional water movement in a partially saturated rigid porous medium is described by a modified form of the Richards equation

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[ K \left( \frac{\partial h}{\partial z} + 1 \right) \right] \quad (1)$$

where  $h$  = water pressure head;  $\theta$  = volumetric water content;  $t$  = time;  $z$  = spatial coordinate (positive upward); and  $K$  = unsaturated hydraulic conductivity.

### Unsaturated Soil Hydraulic Properties

The soil water retention,  $\theta(h)$ , and hydraulic conductivity,  $K(h)$ , functions are given by (van Genuchten 1980)

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m} \quad (2)$$

$$K(h) = rK_s K_r = rK_s S_e^{1/2} [1 - (1 - S_e^{1/m})^m]^2 \quad (3)$$

in which  $\theta_r$  and  $\theta_s$  = residual and saturated water contents; respectively;  $K_s$  = saturated hydraulic conductivity;  $K_r$  = relative hydraulic conductivity;  $\alpha$  and  $n$  = scaling and shape factors, respectively;  $m = 1 - 1/n$ ; and  $S_e$  = effective saturation.

Note that (3) contains an additional scaling parameter  $r$  to account for the effects of solution composition (as determined by the values of pH, SAR and salinity) on the final hydraulic conductivity. The value of  $r$  equals unity under favorable chemical conditions involving optimal pH, SAR and salinity. Although the magnitude of the effects of pH, SAR, and total salinity on  $K(h)$  appears to be soil specific, we included in UNSATCHEM reduction functions calculated for some Californian illitic soils based on the experimental work of McNeal (1968) and Suarez et al. (1984). The overall scaling factor  $r$  is for this purpose divided into two parts as follows:

$$r(\text{pH, SAR, } C_0) = r_1(\text{SAR, } C_0)r_2(\text{pH}) \quad (4)$$

where  $r_1$  reflects the effect of ESP (SAR) and total soil solution salinity,  $C_0$ , on the hydraulic conductivity, while  $r_2$  accounts for the effect of the soil solution pH. The first term is based on a clay-swelling model that treats mixed-ion clays as simple

mixtures of homoionic sodium and calcium clay (McNeal 1974)

$$r_1 = 1 - \frac{\alpha \kappa^b}{1 + \alpha \kappa^b} \quad (5)$$

where  $a$  and  $b$  = empirical parameters; and  $\kappa$  = a swelling factor. The interlayer swelling of soil montmorillonite,  $\kappa$ , is defined in the following way:

$$\kappa = f_{\text{mont}} 3.6 \cdot 10^{-4} \text{ ESP}^* d^* \quad (6)$$

where  $f_{\text{mont}}$  = weight fraction of montmorillonite in the soil;  $d^*$  = adjusted interlayer spacing; and  $\text{ESP}^*$  = adjusted exchangeable sodium percentage. The definition of all terms can be found in McNeal (1968).

The reduction factor,  $r_2$ , for the effect of pH on hydraulic conductivity was calculated from experimental data of Suarez et al. (1984) after first correcting for the adverse effects of low salinity and high exchangeable sodium on  $K(h)$  using the foregoing  $r_1$  value. The effects are attributed to increased negative charge on mineral surfaces with increased pH. The data by Suarez et al. (1984) lead to

$$r_2 = 1 \quad \text{for } \text{pH} < 6.83 \quad (7a)$$

$$r_2 = 3.46 - 0.36 \text{ pH} \quad \text{for } 6.83 \leq \text{pH} \leq 9.3 \quad (7b)$$

$$r_2 = 0.1 \quad \text{for } \text{pH} > 9.3 \quad (7c)$$

In view of differences among soils, the preceding specific relationships (especially parameters  $a$  and  $r_2$ ) are not likely to be accurate predictors of hydraulic conductivity for a generalized model, but they do serve to describe the type of changes that occur in soils during infiltration under various chemical conditions. Thus, for soils of different mineralogy, the parameters need to be characterized along with the hydraulic characteristics given by (2) and (3). The model of McNeal (1968) has been successfully used for a range of soil materials (McNeal 1974), while the model describing the pH effects on hydraulic conductivity was developed only recently by Suarez and Šimůnek (unpublished paper, 1997).

The preceding model describing reductions in the soil hydraulic conductivity due to chemical effects was derived from saturated hydraulic conductivity data. Detailed information on the effects of chemical factors on the unsaturated hydraulic conductivity is not available, and hence we used the same reduction factors over the entire range of pressure heads. The saturated hydraulic conductivity is likely more sensitive to the solution composition than the unsaturated conductivity. As such, it may be possible that reductions in the unsaturated hydraulic conductivity will be somewhat overestimated during unsaturated water flow.

### Solute Transport and Chemical Reactions

The partial differential equation governing one-dimensional chemical transport of the  $k$ th solute component during transient water flow in a variably saturated multicomponent transport system is taken as (Šimůnek et al. 1996)

$$\frac{\partial(\theta c_k)}{\partial t} + \rho \frac{\partial \bar{c}_k}{\partial t} + \rho \frac{\partial \hat{c}_k}{\partial t} = \frac{\partial}{\partial z} \left( \theta D \frac{\partial c_k}{\partial z} - q c_k \right),$$

$$k = 1, 2, \dots, n_s \quad (8)$$

where  $c_k$ ,  $\bar{c}_k$ , and  $\hat{c}_k$  = total dissolved, sorbed, and mineral concentrations of the aqueous component  $k$ , respectively;  $\rho$  = bulk density of the medium;  $q$  = volumetric flux;  $n_s$  = number of aqueous components; and  $D$  = dispersion coefficient. The total concentration of a component  $k$ , defined as the sum of the dissolved, sorbed, and mineral concentrations, is influenced

TABLE 1. Species Considered in Chemical Submodel

Type (1)	Number (2)	Species considered (3)
Aqueous components	7	Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>
Complexed species	10	CaCO <sub>3</sub> <sup>0</sup> , CaHCO <sub>3</sub> <sup>+</sup> , CaSO <sub>4</sub> <sup>0</sup> , MgCO <sub>3</sub> <sup>0</sup> , MgHCO <sub>3</sub> <sup>+</sup> , MgSO <sub>4</sub> <sup>0</sup> , NaCO <sub>3</sub> <sup>0</sup> , NaHCO <sub>3</sub> <sup>0</sup> , NaSO <sub>4</sub> <sup>-</sup> , KSO <sub>4</sub> <sup>-</sup>
Precipitated species	5	CaCO <sub>3</sub> , CaSO <sub>4</sub> ·2H <sub>2</sub> O, MgCO <sub>3</sub> ·3H <sub>2</sub> O, Mg <sub>2</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O, CaMg(CO <sub>3</sub> ) <sub>2</sub>
Sorbed species	4	Ca, Mg, Na, K
CO <sub>2</sub> -H <sub>2</sub> O species	7	H <sub>2</sub> CO <sub>3</sub> <sup>*</sup> , H <sub>2</sub> CO <sub>3</sub> <sup>*</sup> , CO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , H <sup>+</sup> , OH <sup>-</sup> , H <sub>2</sub> O

only by transport processes that act on the solution concentration  $c_k$ . However, the relative fraction of a component in each of the three phases (solution, sorbed, mineral) depends strongly on the specific chemical processes in the system. Therefore, (8) must be augmented with a set of equations describing the various equilibrium or nonequilibrium chemical reactions such as complexation, cation exchange, and precipitation/dissolution.

The chemical submodel in UNSATCHEM is a speciation program that considers cation exchange using "Gapon type" expressions and has provisions for either equilibrium with solid phases or dissolution-precipitation using kinetic expressions. A total of 33 chemical species, listed in Table 1, are considered. The model allows for precipitation of gypsum, calcite, sepiolite, hydromagnesite, and nesquehonite whenever the calculated solution composition exceeds saturation for these phases. If any of these phases are specified as present in the soil, the model can force the solution to saturation.

Partitioning between the solution and surface phases (the fourth group in Table 1) was described in UNSATCHEM with the Gapon equation (White and Zelazny 1986)

$$\bar{K}_{ij} = \frac{\bar{c}_i^{y+} (c_j^{x+})^{1/x}}{c_j^{x+} (c_i^{y+})^{1/y}} \quad (9)$$

where  $y$  and  $x$  are the valences of species  $i$  and  $j$ , respectively,  $\bar{K}_{ij}$  is the Gapon selectivity coefficient, and the adsorbed concentration is expressed in mol.kg<sup>-1</sup> of soil. We assumed that the cation exchange capacity (CEC) was constant and independent of pH.

Precipitation-dissolution of calcite can be optionally treated using either equilibrium or kinetic expressions, while dissolution of dolomite is always treated as a kinetic process (Šimůnek and Suarez 1994). The precipitation-dissolution of equilibrium solids was expressed in terms of solubility products  $K_{sp}$ .

$$K'_{sp} \geq \prod_j (c_j^{v_j}) \quad (10)$$

in which the stoichiometric coefficient  $v_{ij}$  gives the molar fraction of component  $j$  in solid  $i$ . Finally, the species in the last group of Table 1 are represented by Henry's Law, the first and second dissociation equation for carbonic acid, the dissociation equation for water, and the charge balance equation. The entire system of equations is closed by an electric charge balance equation that allows calculation of pH.

### ANALYSIS OF RECLAMATION OPTIONS

Numerous methods have been proposed for reclaiming sodic soils. Among these are the application of gypsum to the soil surface (Keren 1990) or in the irrigation water (Ayers and Westcot 1985), incorporation of gypsum into the upper soil profile ("Diagnosis" 1954), the addition of acid to calcareous soil (Overstreet et al. 1951; Yahia 1975; Prather et al. 1978), leaching calcareous soils with high quality water, and addition

of acidic organic matter or waste products into the profile to reduce pH and enhance CO<sub>2</sub> production and dissolution of calcite (Jones et al. 1993). In the simulations examined in the following we compare several of these reclamation practices, both with and without consideration of the chemical effects on the soil hydraulic properties.

The examples assume that the soil surface is flooded with water, with the water kept at a constant level of 1 cm above the soil surface. Free drainage was used as the bottom boundary condition. The initial pressure head condition was -500 cm and we used the soil hydraulic properties of a hypothetical loam soil (Šimůnek and Suarez 1994). The soil hydraulic parameters in van Genuchten's (1980) formulation [Eqs. (2) and (3)] were as follows:  $\theta_r = 0.000$ ,  $\theta_s = 0.480$ ,  $n = 1.592$ ,  $\alpha = 0.015 \text{ cm}^{-1}$ , and  $K_s = 60.48 \text{ cm/d}^{-1}$ . The bulk density of the soil was taken as  $1.3 \text{ g/cm}^3$ .

The calculations were run at a constant temperature of 20°C and at either a variable (model-predicted) or a constant CO<sub>2</sub> partial pressure. Model-predicted CO<sub>2</sub> concentrations were obtained with an optimal CO<sub>2</sub> production value of  $0.007 \text{ m}^3 \text{ m}^{-2} \text{ d}^{-1}$ . We assumed that all CO<sub>2</sub> production was the result of soil respiration (decay of the soil organic matter). Production was exponentially distributed within the soil profile, with a maximum at the surface. The CO<sub>2</sub> production values were adjusted according to environmental conditions as described in Suarez and Šimůnek (1993). The CO<sub>2</sub> content in the atmosphere was used as the upper boundary condition for the soil as well as for the CO<sub>2</sub> concentration of the infiltrating water. A zero CO<sub>2</sub> concentration gradient was imposed at the bottom of the soil profile.

The solution composition of the water initially present in the soil profile was assigned to be that of the following highly sodic soil water system:  $\text{Ca}_T = 0.2$ ,  $\text{Mg}_T = 0.2$ ,  $\text{Na}_T = 4.8$ ,  $\text{Cl}_T = 4.8$ , and alkalinity =  $0.4 \text{ mmol}_e \text{ L}^{-1}$ . The cation exchange capacity was set at  $200 \text{ mmol}_e \text{ kg}^{-1}$  and the ESP at 60 ( $\text{Ca} = 40.0$ ,  $\text{Mg} = 40.0$ ,  $\text{Na} = 120.0 \text{ mmol}_e \text{ kg}^{-1}$ ). The Gapon selectivity coefficients for Ca-Na and Ca-Mg exchange were set to  $\bar{K}_{13} = 1.158$  and  $\bar{K}_{12} = 0.896$  (Wagenet and Hutson 1987), respectively. For calcareous soils we assumed that calcite was present at a concentration of  $1,000 \text{ mmol}_e \text{ kg}^{-1}$  of soil (about 0.5% by weight). Four different irrigation water compositions were used: high-quality dilute irrigation water, irrigation water high in Ca and SO<sub>4</sub> (almost gypsum-saturated), and two acidified waters—one at pH = 2.05 and the other at pH = 1.09. The solution compositions of the four irrigation water types are presented in Table 2.

Reclamation was attempted in seven different ways. In the first and second cases, high-quality and gypsum-saturated water, respectively, were applied to the soil without consideration of calcite dissolution. The first strategy is inappropriate for the reclamation of sodic soils that do not contain gypsum or calcite, since high-quality water has an insufficient supply of Ca for replacing the exchangeable sodium ions. We use the first case only as a reference to compare simulations, especially for showing the effects of calcite dissolution on reclamation. The

**TABLE 2. Solution Composition of Irrigation Waters and Water Initially in Soil Profile**

Water type (1)	Element or Compound (mmol <sub>e</sub> L <sup>-1</sup> )					Alkalinity (7)
	Ca (2)	Mg (3)	Na (4)	Cl (5)	SO <sub>4</sub> (6)	
Initially present in soil	0.2	0.2	4.8	4.8	0.0	0.4
High-quality (dilute) water	1.5	0.5	2.0	1.0	2.5	0.5
Gypsum-saturated water	32.0	0.5	2.0	1.0	33.0	0.5
Acidified water I	1.5	0.5	2.0	3.0	11.0	-10.0
Acidified water II	1.5	0.5	2.0	93.0	11.0	-100.0

**TABLE 3. Summary of Reclamation Strategies and Considered Conditions**

Reclamation strategy (1)	Type of irrigation water (2)	Amendments (3)
1	dilute water	no amendments
2	gypsum-saturated water	no amendments
3	dilute water	gypsum in top soil
4	dilute water	calcite in soil, constant CO <sub>2</sub>
5	dilute water	calcite in soil, elevated CO <sub>2</sub>
6	acidified water I	calcite in soil, constant or elevated CO <sub>2</sub>
7	acidified water II	calcite in soil, constant or elevated CO <sub>2</sub>

second reclamation strategy involving gypsum-saturated water has been recommended primarily as a cost-effective method when the soil is still in production and improvements in soil properties are desired. This second case is also closely comparable to the often recommended practice of applying gypsum to the soil surface (Keren 1990) and was for a long time the most prevalent reclamation practice ("Diagnosis" 1954). In the third example, high-quality water was applied to a soil where gypsum was incorporated into the top 20 cm of the soil profile—again without consideration of calcite dissolution. This reclamation method has been frequently recommended especially when a high ESP exists in the subsoil ("Diagnosis" 1954; Ayers and Westcot 1985).

The fourth case, also involving high-quality irrigation water, assumes that the soil solution is in equilibrium with calcite and that the CO<sub>2</sub> concentration throughout the reclamation process changes linearly from the atmospheric equilibrium value at the soil surface (0.035%) up to 2% at the bottom of the soil profile. This method evaluates leaching with calcite, an amendment that is generally considered to be insufficiently soluble to affect sodic soil reclamation. The fifth example also evaluates leaching with calcite, except that the simulation now uses model-predicted CO<sub>2</sub> concentrations. The soil should be at or close to the full soil water saturation during the ponded reclamation process, and the CO<sub>2</sub> concentrations hence are expected to be elevated. We will show that the increased CO<sub>2</sub> concentrations significantly influence both the dissolution of calcite and the value of the soil pH, with both variables having important consequences for the reclamation process. Calcite dissolution can also be enhanced by applying acidic compounds such as sulphuric acid or acid-forming amendments such as sulfur, iron sulfate, and pyrites ("Diagnosis" 1954) to the soil or the irrigation water. In the sixth and seventh reclamation practices, water at two different acid concentrations were applied to the surface of the calcareous soil.

A summary of the different reclamation strategies is given in Table 3. Each reclamation strategy was evaluated at least twice, once with and once without consideration of the chemical effects on soil hydraulic properties. Although UNSATCHEM allows for a kinetic description of the calcite dissolution process, both cation exchange and amendment dissolution were treated as instantaneous processes in the presented calculations.

## RESULTS AND ANALYSIS

A summary of the simulation results, including the time needed for complete water saturation of the soil profile and the time and amount of water needed to reclaim the soil profile, is given for all reclamation strategies in Table 4. Fig. 1 shows calculated pressure head profiles at different times for the first reclamation strategy, i.e., the infiltration of high-quality water into a sodic soil profile without using any reclamation amendments. Assuming no reductions in the soil hydraulic conductivity due to chemical factors, the water infiltrates in

less than 0.5 d to the bottom of the profile [Fig. 1(a)]. In contrast, when a reduction in the soil hydraulic conductivity due to high initial sodium concentration is considered, the moisture front moves extremely slowly throughout the soil. The moisture front now reaches the bottom of the soil profile (depth of 100 cm) after almost one year [Fig. 1(b)].

Distributions of the hydraulic conductivity throughout the soil column at different times are also presented in Fig. 1. If the chemical effects on  $K$  are ignored, the hydraulic conduc-

tivity quickly reaches the maximum  $K$ , value of 60.48 cm/d when the soil profile becomes saturated [Fig. 1(c)]. In contrast, when chemical effects are considered, the initial hydraulic conductivities are extremely low due to the high ESP and the relatively low salinity in the profile [Fig. 1(d)]. The hydraulic conductivity gradually increases with time but still remains less than 1 mm/d after two years of infiltration. As a consequence of the low hydraulic conductivity, infiltration is greatly reduced and reclamation is virtually impossible. This simulation is consistent with observations that it is usually not possible to infiltrate dilute water into a soil with a high ESP. Note that after 238 years, when reclamation of the top layer is complete, the hydraulic properties are still very much reduced because of the use of dilute water for the reclamation process. We emphasize that the simulation results in Fig. 1 cannot be generalized because the reclamation process depends on the chemical composition of the irrigation water and the assumed hydraulic conductivity values.

Fig. 1(e) shows the SAR distributions with depth without considering reductions in the soil hydraulic conductivity. When no reductions in  $K$  are considered, it takes about 60 d to reclaim 50 cm and about 120 d to reclaim the entire soil profile with dilute water. Note that the SAR front is relatively sharp. Reclamation took about 250 times longer than the time needed for the water to infiltrate [compare Figs. 1(a) and 1(e)]. Nonetheless, reclamation after about 120 d could be considered acceptable were it not for the excessive amount of water required (7,260 cm as shown in Table 4). When reductions in the hydraulic conductivity are considered, full reclamation of the soil profile is achieved only after about 238 years [Fig. 1(f)]. Note that now the SAR fronts are not sharp. Water flow in this simulation is sufficiently slow so that diffusion becomes an important component in the solute transport process. If one were to consider the effects of evaporation, water requirements

TABLE 4. Summary of Reclamation Results

Reclamation strategy (1)	Hydraulic conductivity reduction (2)	CO <sub>2</sub> dynamics (3)	Time to profile saturation (d) (4)	Time to profile reclamation (d) (5)	Amount of infiltrated water (cm) (6)
1	no	NA	0.48	120	7,260
	yes	NA	358	86,870	7,230
2	no	NA	0.48	10	610
	yes	NA	15.3	195.6	559
3	no	NA	0.48	8	488
	yes	NA	2	116.5	470
4	no	constant	0.48	16	972
	yes	constant	100	397.5	956
5	no	elevated	0.48	16	972
	yes	elevated	10	91	600
6	no	constant	0.48	10	609
	yes	constant	29	149.5	634
7	no	elevated	0.48	10	609
	yes	elevated	6.4	64.2	485
7	no	constant	0.48	3.5	216
	yes	constant	3.5	15.5	199
	no	elevated	0.48	3.5	216
	yes	elevated	3.2	15.5	197

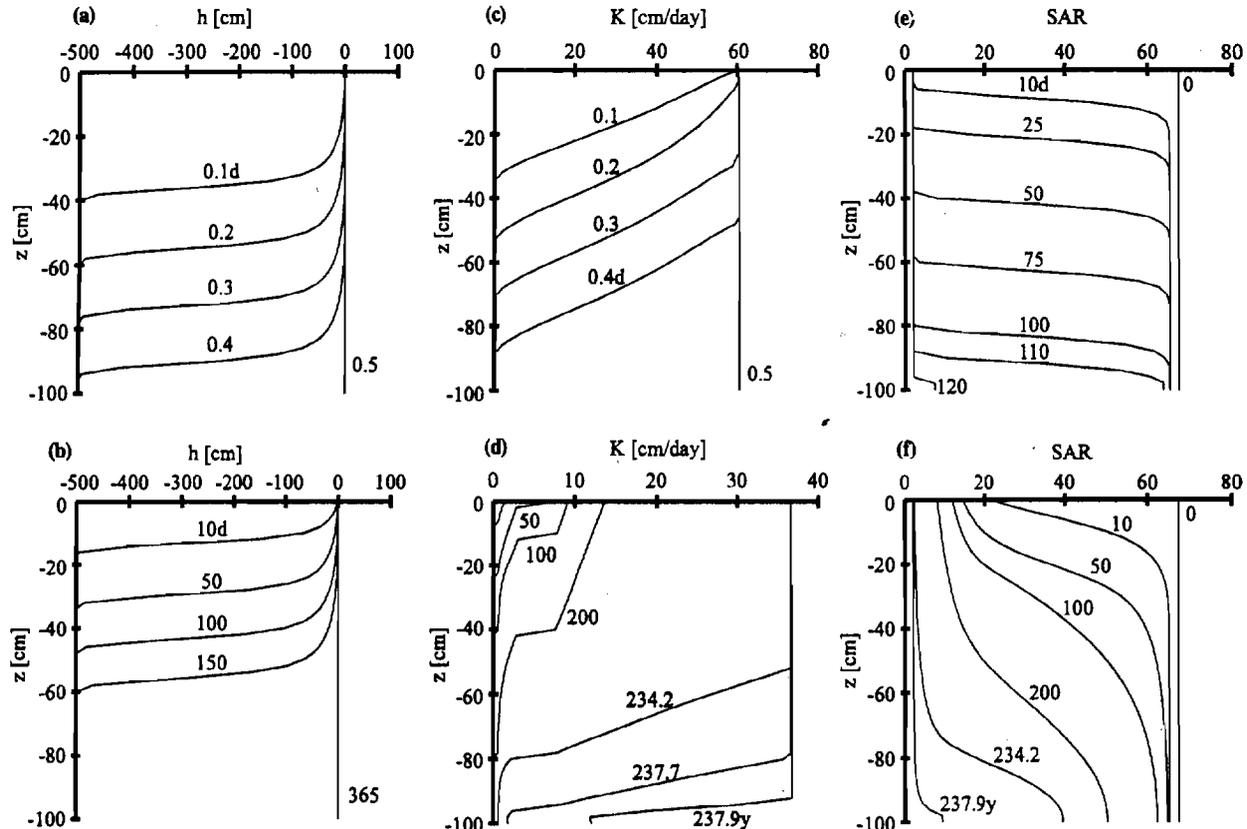


FIG. 1. First Reclamation Strategy (Irrigation with High-Quality Water and No Amendment): (a) Pressure Head Profiles without Consideration of  $K$  Reduction; (b) Pressure Head Profiles with Consideration of  $K$  Reduction; (c) Hydraulic Conductivity Profiles without Consideration of  $K$  Reduction; (d) Hydraulic Conductivity Profiles with Consideration of  $K$  Reduction; (e) Sodium Adsorption Ratio without Consideration of  $K$  Reduction; (f) Sodium Adsorption Ratio with Consideration of  $K$  Reduction

would be much greater. Clearly, reclamation scenarios using dilute infiltration water in the absence of calcite or gypsum dissolution are not practical, especially when the chemical effects on infiltration are considered. The preceding two simulations show that failure to consider chemical effects on hydraulic properties results in small errors in the predicted quantities of water and the amount of Ca needed for reclamation. More importantly, the time required for reclamation cannot be accurately simulated without consideration of the chemical effects on the soil hydraulic properties.

The second reclamation strategy represents infiltration of gypsum-saturated water into the soil. In the absence of any chemical effects, the soil hydraulic conductivity distributions are the same as for the previous simulation [Fig. 1(c)]. Fig. 2(a) shows the hydraulic conductivity profiles with consideration of chemical effects on  $K$ . The high electrolyte content of the water now increases the hydraulic conductivity of the soil from 0.05 to about 20 cm/d immediately after infiltration. The hydraulic conductivity of the upper layers improves as the cation exchange process progresses. However, the infiltration rate itself does not increase because of the lower conductivity of the deeper layers in the soil profile. The dramatic effect of reclamation on the infiltration rate,  $q_0$ , can be seen in Fig. 2(b). The infiltration rate after reclamation is completed is above 50 cm/d. The actual hydraulic conductivity in the surface layers after 150 d [Fig. 2(a)] does not quite reach the maximum value of 60.48 cm/d because of the near surface pH being above its optimum value. Since the deeper layers are at optimum pH, their  $K_s$  values are at their maximum (60.48 cm/d), even though  $K$  itself is below 60 cm/d (the soil is not completely saturated below the surface layers).

Fig. 2(c) shows that for the second reclamation strategy without consideration of chemical effects on the hydraulic conductivity, complete reclamation would have been predicted after only 10 d. This is much faster than reclamation with dilute water [Fig. 1(e)] and is caused by the high concentration of Ca in the irrigation water. Again, this simulation is not realistic because the effects of chemical processes were not considered. Taking chemical effects on  $K$  into account will lead to complete reclamation after almost 200 d [Fig. 2(d)]. Notice from Fig. 2(d) that there are two distinctive fronts in the SAR profiles. The first fast front reaches the bottom of the soil profile after about 10 d and corresponds to the movement of inert tracers. The second front corresponds to the Ca-Na exchange front and moves much slower, reaching the bottom of the soil profile after about 200 d. Application of gypsum-saturated water or surface application of gypsum is thus a feasible reclamation method under certain instances, particularly when the ESP is not very high or when the maximum  $K_s$  values are large. This strategy may not always be acceptable for soils with lower optimum saturated hydraulic conductivities or deeper sodic horizons that would take longer to reclaim.

Reclamation is often accomplished by incorporating gypsum into the upper layers of the soil and subsequent leaching (the third reclamation strategy). Fig. 3(a) shows hydraulic conductivity profiles for the simulation that considers chemical effects on  $K$ . Incorporation of gypsum results in an immediate increase in hydraulic conductivity in all layers to which gypsum was added. The infiltration rate [Fig. 3(b)] is initially high as the water rapidly saturates the upper layers, followed by a sharp decrease as the soil profile becomes saturated. A rapid increase of the infiltration rate occurs after about 115 d when reclamation is completed. Incorporation of gypsum results in a higher salinity at or near the reclamation front, thus causing the infiltration rate during reclamation to be higher. The final infiltration rate in this simulation [Fig. 3(b)] is slightly slower than when gypsum-saturated water was used [Fig. 2(b)]; this is because the surface gypsum has completely dissolved (down

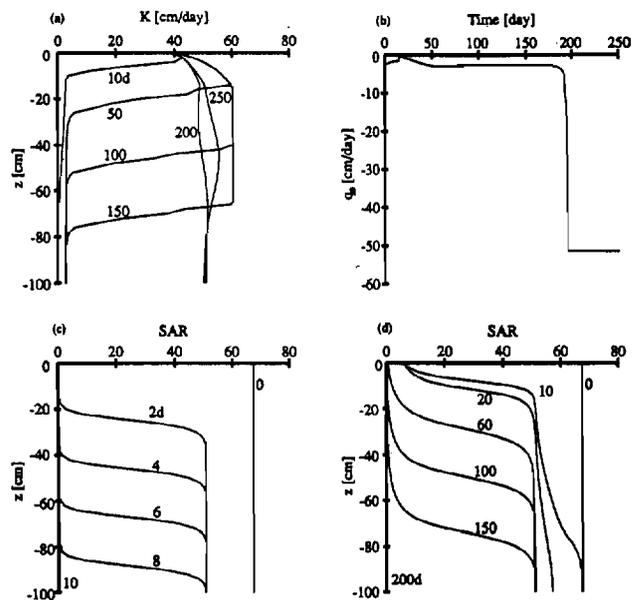


FIG. 2. Second Reclamation Strategy (Irrigation with Gypsum-Saturated Water): (a) Hydraulic Conductivity Profiles; (b) Infiltration Rate; (c) Sodium Adsorption Ratio without Consideration of  $K$  Reduction; (d) Sodium Adsorption Ratio with Consideration of  $K$  Reduction

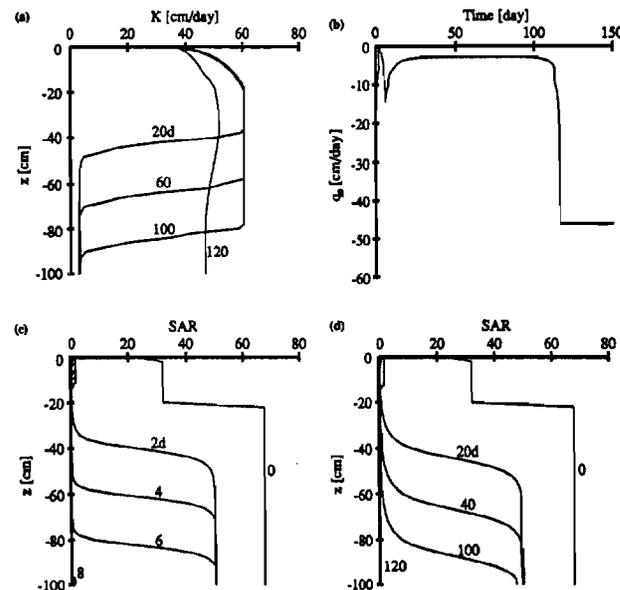


FIG. 3. Third Reclamation Strategy (Gypsum Reclamation Incorporated in Top 20 cm): (a) Hydraulic Conductivity Profiles Considering Chemical Effects on  $K$ ; (b) Infiltration Rate Considering Chemical Effects on  $K$ ; (c) Sodium Adsorption Ratio without Consideration of  $K$  Reduction; (d) Sodium Adsorption Ratio with Consideration of  $K$  Reduction

to 10 cm depth) and the surface layer solution reflects the dilute irrigation water composition. Changing from gypsum-saturated water to dilute irrigation water would be expected once reclamation is completed, thus causing the two infiltration rates to become the same.

Incorporation of gypsum into the upper 20 cm of the profile results in immediate partial reclamation of that part of the profile since the UNSATCHEM model assumes equilibrium reactions between gypsum, surface species, and solution. This is shown in Fig. 3(c), which presents SAR distributions when no reductions in the hydraulic parameters are considered. The SAR initially decreased from 68 to 32 because of the presence of gypsum. Later, reductions in SAR were caused by leaching of Na from the soil profile and further dissolution of gypsum.

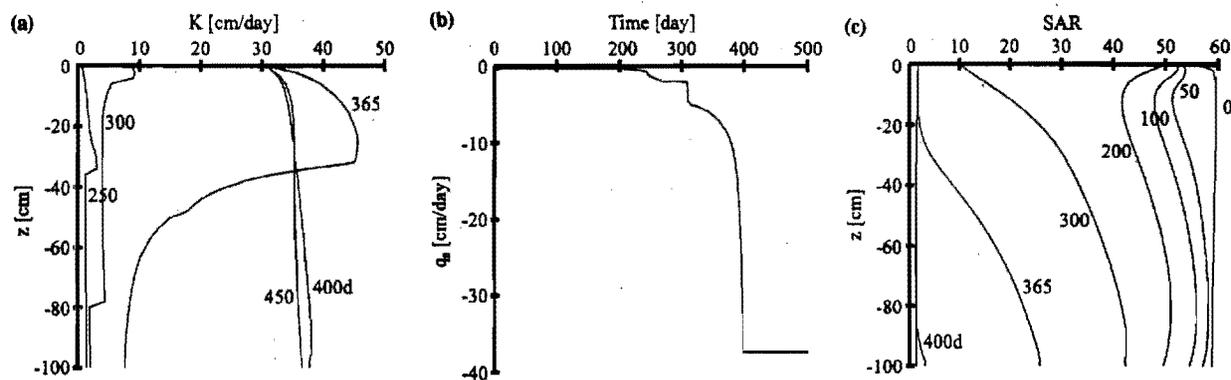


FIG. 4. Fourth Reclamation Strategy (Reclamation with Calcite throughout Profile, Constant  $\text{CO}_2$ , and Consideration of Reduction in  $K$ ): (a) Hydraulic Conductivity Profiles; (b) Infiltration Rate; (c) Sodium Adsorption Ratio Profiles

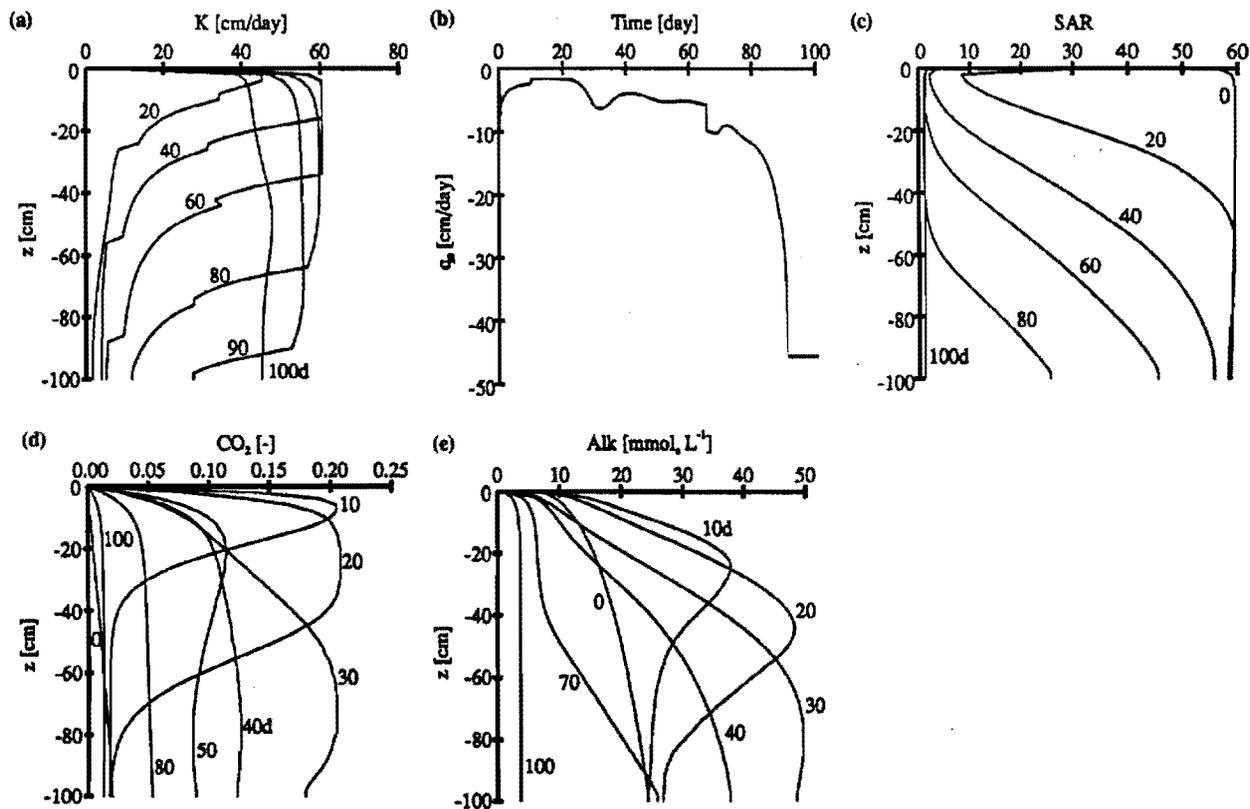


FIG. 5. Fifth Reclamation Strategy (Reclamation with Calcite throughout Profile, Model-Predicted  $\text{CO}_2$ , and Consideration of Reduction in  $K$ ): (a) Hydraulic Conductivity; (b) Infiltration Rate; (c) Sodium Adsorption Ratio; (d)  $\text{CO}_2$ ; (e) Alkalinity

The major difference in reclamation with [Fig. 3(d)] and without [Fig. 3(c)] considering chemical effects on  $K$  is time. Reclamation while considering chemical effects was simulated as requiring 116 d versus 8 d without considering chemical effects on the hydraulic properties. Again, as with reclamation with gypsum-saturated water, the reclamation processes and decisions regarding the economic viability of a particular strategy cannot be made without considering the time requirements involved (as well as the amount of water and the amount and cost of amendments). Reclamation by incorporating gypsum into the soil profile, as compared to surface application of gypsum or gypsum-saturated water, results in a reduction in time from 200 d to 116 d and a reduction in water requirements from 559 to 470 cm of water (see Table 4). A decision as to which strategy to use must also consider the energy and labor costs of mixing gypsum into the upper soil layers.

Traditionally calcite (which is almost always present in sodic soils of arid regions) has been viewed as not being sufficiently soluble to affect sodic soil reclamation. In the following (fourth) strategy we infiltrated dilute water and considered

that  $\text{CO}_2$  pressures in the soil profile increased linearly from atmospheric at the surface to 2 kPa (2%) at 100 m. As shown in Fig. 4(a), the hydraulic conductivity increased slowly with time and relatively uniformly with depth. Adequate infiltration rates did not occur until after about 400 d [Fig. 4(b)], at which time they stabilized at 38 cm/d. In contrast to reclamation with gypsum, the calcite reclamation front, shown in Fig. 4(c), was not sharp; it took 400 d to reclaim the entire soil profile. The reclamation time and quantity of water (considering the chemical effects on soil hydraulic properties) was predicted to be approximately two times greater than with gypsum reclamation (see Table 4). These simulations suggest that reclamation with calcite may be feasible.

Consideration of  $\text{CO}_2$  production and transport and its effect on calcite solubility (reclamation strategy five), dramatically affects the preceding conclusions regarding reclamation with calcite. Fig. 5(a) shows that the hydraulic conductivity increased relatively rapidly, reaching a maximum value after 100 d. These changes are more rapid than the corresponding values shown in Fig. 2(a) for reclamation with gypsum-saturated wa-

ter. Several discontinuities in the hydraulic conductivity as apparent from Fig. 5(a) were caused by the discontinuity of the McNeal reduction model for different ESP levels. The infiltration rate was predicted to increase gradually with time, as shown in Fig. 5(b), reaching a maximum value after 91 d. This reclamation time was only slightly less than that obtained for gypsum (Table 4). However, the initial increase in the infiltration rate was considerably less than with other reclamation strategies. For example, after 40 d the infiltration rate is 5 cm/d; this rate is not reached until 185 d with gypsum-saturated water [Fig. 2(b)] and 110 d when gypsum was incorporated in the upper part of the profile [Fig. 3(b)].

The SAR values shown in Fig. 5(c) indicate that Na exchange was complete after about 90 d. Reclamation is traditionally considered complete when the ESP becomes less than 15. A more useful definition for complete reclamation may be whenever sufficient exchange has occurred so that the infiltration rate is above a required minimum value. This minimum value is necessary to meet water demands of the crop and provide adequate leaching. Using these criteria, leaching could already be considered adequate after 40 d. The effectiveness of calcite in this instance is the result of  $\text{CO}_2$  production after ponded conditions when diffusion is restricted because of water saturation. As shown in Fig. 5(d),  $\text{CO}_2$  concentrations increased rapidly over the first 25 d. As water flow increased,  $\text{CO}_2$  concentrations decreased due to transport with the flowing water. At  $\text{CO}_2$  partial pressures of 10–20 kPa, which are common in ponded soils in the presence of organic matter, calcite solubility is greatly enhanced. Calcite solubility is further enhanced by removal of Ca from solution by exchange with adsorbed Na.

The alkalinity of soil water, shown in Fig. 5(e), provides a direct measure of the amount of calcite dissolved, since irrigation water itself contains almost no alkalinity. During the

initial stage of reclamation, 20–50  $\text{mmolL}^{-1}$  of calcite was dissolved. Thus, in this case, calcite supplied more Ca than did the reclamation strategy with gypsum saturated water. This strategy was even more effective than was gypsum reclamation when gypsum was incorporated into the upper 20 cm of the profile. This conclusion is based on the time needed for reclamation, although somewhat more water was required (see Table 4). The reason that calcite was so effective was that, unlike gypsum, the calcite amendment was present throughout the profile. As a result, all locations in the profile were able to dissolve additional Ca as exchange occurred. A similar enhanced dissolution process occurred during gypsum reclamation where the gypsum was present (since gypsum is more soluble than calcite). However, no further Ca source was available below the upper 20 cm zone. The relative effectiveness of gypsum or calcite with enhanced  $\text{CO}_2$  depends very much on the anion present in the soil or irrigation water. For example, calcite dissolution would be severely reduced if the irrigation water was of high alkalinity. Similarly, gypsum is not very effective when large amounts of dissolved sulfate are present.

The sixth strategy examined involved reclamation by application of dilute water acidified to pH 2.05 (net acidity of 10  $\text{mmolL}^{-1}$ ) in a calcareous soil. The SAR profiles for simulations with constant  $\text{CO}_2$  and model-predicted  $\text{CO}_2$  are shown in Figs. 6(a) and (b), respectively. As shown in these figures and in Table 4, consideration of  $\text{CO}_2$  predicted by the model resulted in reclamation being complete in 64 d versus 150 d when a constant  $\text{CO}_2$  pressure was simulated. The data in Table 4 also show that 20% less water was required when model-predicted  $\text{CO}_2$  values were used in the simulations. Application of acid reduced the time and water requirements by about 30% as compared to the fifth reclamation strategy (calcite— $\text{CO}_2$ ). The acid served to increase the initial Ca concentration and improve the initial infiltration rates (data not shown). All calcite in the top 5 cm of the profile was dissolved by the acid.

The seventh strategy was application of pH 1.09 dilute water to a calcareous soil. The SAR in this case decreased rapidly, as shown in Figs. 7(a) and (b), for constant and model-predicted  $\text{CO}_2$  simulations, respectively. In this strategy the acid was sufficiently concentrated that differences due to  $\text{CO}_2$  could be neglected. Comparison of the data in Table 4 shows that the low pH dilute irrigation water strategy was overall the most effective in terms of the least amount of time and water required. This reclamation practice would have been even more effective if more calcite had been assumed to be present in the profile. As shown in Fig. 7(c), infiltration of acid resulted in dissolution of all calcite in the soil down to a depth of 15 cm. Addition of acid is feasible as a reclamation strategy only if sufficient calcium carbonate is present in the soil. This

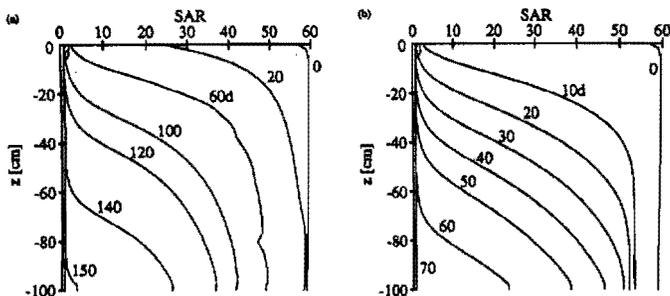


FIG. 6. Sixth Reclamation Strategy (Reclamation by Infiltration of Acid Water at pH 2.05 into Calcareous Soil and Consideration of Reduction in  $K$ ): (a) Sodium Adsorption Ratio Profiles with Constant  $\text{CO}_2$ ; (b) Sodium Adsorption Ratio Profiles with Model-Predicted  $\text{CO}_2$

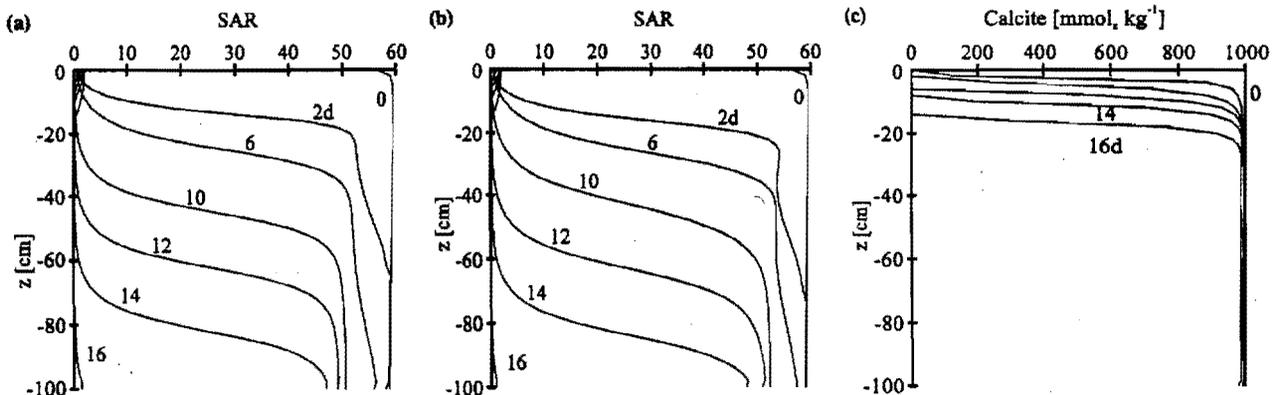


FIG. 7. Seventh Reclamation Strategy (Application of Acid Water at pH 1.09 into Calcareous Soil and Consideration of Reduction in  $K$ ): (a) Sodium Adsorption Ratio with Constant  $\text{CO}_2$ ; (b) Sodium Adsorption Ratio with Model-Predicted  $\text{CO}_2$ ; (c) Calcite Profiles with Time

is because of the undesirable effects of leaving the soil at a very low pH, as occurred in the upper portion of the profile (pH below 5.0). The conclusion that acid addition to a calcareous soil is more effective than application of gypsum is consistent with observations in both column studies and field experiments (Overstreet et al. 1951; Yahia et al. 1975; Prather et al. 1978). Our simulations hence provide a conceptual basis for those observations.

Table 4 also summarizes reclamation results for cases that we do not discuss further, notably reclamation strategies six and seven without consideration of the effects of solution composition on soil hydraulic parameters.

## CONCLUSIONS

Reclamation simulations using the UNSATCHEM model resulted in recommendations that, qualitatively, are in general agreement with field observations. We demonstrated the critical importance of including the effects of solution composition on soil hydraulic parameters in the model predictions. Only models with this feature can successfully estimate the time required for the reclamation process. This information is critical to decisions about the choice of strategy to be employed and its economic viability. Estimates of the quantities of water, as well as the amounts of reclamation materials (and depth of incorporation) to be applied, are also important reclamation parameters. We have shown that calculation of these parameters is dependent upon the CO<sub>2</sub> concentration, thus requiring a model capable of predicting CO<sub>2</sub> concentrations under dynamic field conditions. Flooding, combined with CO<sub>2</sub> production, elevates CO<sub>2</sub> concentrations in the root zone and results in a very effective reclamation practice. This conclusion is consistent with previously reported field experiments. Application of acid or dilute water to calcareous soil with elevated CO<sub>2</sub> concentrations, incorporating gypsum into the top of the soil profile, and application of gypsum-saturated water were shown to be decreasingly less effective reclamation strategies.

The sodic soil reclamation model is expected to be especially useful for situations where high alkalinity or high sulfate waters prevent generalizations about relative solubility of the amendments. For each individual situation it is recommended to run a series of simulations and evaluate the results using the following criteria: quantity of water, quantity of amendment, and time required for reclamation.

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## APPENDIX II. NOTATION

The following symbols are used in this paper:

$a, b$  = empirical parameters in hydraulic conductivity reduction function;  
 $C_0$  = total soil solution salinity ( $\text{ML}^{-3}$ );  
 $c_k, \bar{c}_k, \hat{c}_k$  = total dissolved ( $\text{ML}^{-3}$ ), sorbed ( $\text{MM}^{-1}$ ), and mineral ( $\text{MM}^{-1}$ ) concentrations of aqueous component  $k$ , respectively;  
 $D$  = dispersion coefficient ( $\text{L}^2\text{T}^{-1}$ );  
 $d^*$  = adjusted interlayer spacing (L);  
ESP = exchangeable sodium percentage;  
ESP\* = adjusted exchangeable sodium percentage;  
 $f_{\text{mont}}$  = weight fraction of montmorillonite in soil;  
 $h$  = pressure head (L);  
 $K$  = unsaturated hydraulic conductivity ( $\text{LT}^{-1}$ );  
 $K_{\text{sp}}$  = solubility products of mineral phase;  
 $K_r, K_s$  = relative and saturated ( $\text{LT}^{-1}$ ) hydraulic conductivities, respectively;  
 $K_y$  = Gapon selectivity coefficient;

$n$  = parameter of the retention curve;  
 $n_s$  = number of aqueous components;  
 $q$  = volumetric flux ( $\text{LT}^{-1}$ );  
 $r$  = scaling factor that represents effect of solution composition on hydraulic conductivity;  
 $r_1$  = scaling factor that represents effect of ESP and dilution of solution on hydraulic conductivity;  
 $r_2$  = scaling factor that represents effect of soil solution pH on hydraulic conductivity;  
 $S_e$  = effective saturation;  
 $t$  = time (T);  
 $z$  = spatial coordinate (L) (positive upward);  
 $\alpha$  = parameter of retention curve ( $\text{L}^{-1}$ );  
 $\theta$  = volumetric water content ( $\text{L}^3\text{L}^{-3}$ );  
 $\theta_r, \theta_s$  = residual and saturated water contents, respectively ( $\text{L}^3\text{L}^{-3}$ );  
 $\kappa$  = swelling factor;  
 $\nu_{ij}$  = stoichiometric coefficient that gives molar fraction of component  $j$  in solid  $i$ ; and  
 $\rho$  = bulk density of porous medium ( $\text{ML}^{-3}$ ).