

Mechanism and numerical simulation of multicomponent solute transport in sodic soils reclaimed by calcium sulfate

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Abstract The mechanism for reclaiming sodic soils using calcium sulfate (CaSO_4) could provide a theoretical basis for the field application of CaSO_4 substitutes, including the by-products of flue gas desulfurization (BFGD), fly ash, and phosphorus gypsum. In this study, Ca^{2+} application experiment was conducted to analyze the dynamic changes of the cations in the reclamation of sodic soils with CaSO_4 . A multicomponent solute transport model (UNSATCHEM) that considers ion adsorption exchange and dynamic changes in the soil's hydraulic conductivity was subsequently used to simulate and predict the movement of ions. The Ca^{2+} application experiment consisted of four treatments with four CaSO_4 concentrations (0.5, 1, 1.5, and 2 g L^{-1}). When the Ca^{2+} concentrations in the supplied water were 14.71, 22.06, and 29.41 mmol L^{-1} , Ca^{2+} achieved penetration, and this process was faster when the Ca^{2+} concentration in the supplied water was higher. Ca^{2+} did not achieve penetration when the Ca^{2+} concentration was 7.35 mmol L^{-1} . UNSATCHEM was able to simulate the transportation mechanism of Ca^{2+} and Na^+ in the soil solution in the Ca^{2+} application experiment, the adsorption

and exchange between the Na^+ in the soil colloid and Ca^{2+} in the soil solution, and the precipitation and dissolution of CaSO_4 with a high degree of accuracy. Sodic soil reclamation with CaSO_4 was not a short-term process. Compared with applying CaSO_4 only once, applying CaSO_4 in batches decreased the accumulation of soil salts and promoted its dissolution.

Keywords Sodic soils · Soil reclamation · Calcium sulfate · Numerical simulation · Multicomponent solute transport

Introduction

Typical sodic soils contain an excess of exchangeable sodium ($\overline{\text{Na}^+}$) in the soil colloids, and the soluble carbonates are in the form of Na_2CO_3 and NaHCO_3 . This results in soil with a high pH (>8.5), clay dispersion, soil swelling, and poor overall physical properties (Suarez et al. 1984; Gupta and Abol 1990; Qadir et al. 2000). It is necessary to improve the physical and chemical properties of soil for both soil reclamation and soil erosion control. The key to reclamation is to remove the $\overline{\text{Na}^+}$ and replace it with more favorable calcium ions in the topsoil (Qadir et al. 2001; Ranjbar and Jalali 2011). Historically, sodic soils have been reclaimed with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Using CaSO_4 can only be justified economically by the yield response in reclaiming sodic soils, usually over several seasons (Gupta and Abol 1990). In recent years, with the advent of alternatives, such as the by-products of flue gas desulfurization (BFGD), fly ash, and phosphorus gypsum, the mechanism for reclaiming sodic soils using calcium sulfate has again become an interesting research field

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(Chun et al. 2001; Pandey et al. 2011; Wang et al. 2012, 2013; Singh et al. 2012b).

The low solubility of calcium salt means that it is easily precipitated in soil solutions, for example, CaCO_3 and CaSO_4 , which also increases the relative proportion of Na^+ in the soil exchange phase. Because the Na^+ enhances the dissolution of CaSO_4 , especially under the conditions of crop growth, the organic and inorganic acids formed by organic matter decomposition and biological and chemical interaction play a larger role in promoting the dissolution of CaSO_4 . The dissolution of powdered CaSO_4 is enough to relieve or prevent soil dispersion and also plays a positive role in maintaining the stability of the soil structure (USDA 1954; Gill et al. 2009; Sahin and Anapali 2005). Therefore, a series of complex physical and chemical processes, including ion adsorption exchange and precipitation dissolution, are generated when sodic soils are reclaimed by CaSO_4 . The soil solution concentration, pH, sodium adsorption ratio (SAR), and exchangeable sodium percentage (ESP) have strong effects on the soil's hydraulic conductivity, which decreases as the ESP increases and the soil solution concentration decreases (Singh et al. 2012a; Tejada et al. 2006). Therefore, the soil hydraulic conductivity changes dynamically during sodic soil reclamation by CaSO_4 (McNeal 1968; Sahin et al. 2011; Gharaibeh et al. 2009).

Numerous analytical and numerical models are now available to predict solute transport processes between the soil surface and the groundwater table. These models are typically based on the numerical solutions of Richard's equation for variably saturated flow and analytical or numerical solutions of the Fickian equation based on the convection–dispersion equation for solute transport (Ciftci et al. 2012; Liu et al. 2009). Deterministic solutions of these classical equations will no doubt remain important for predicting water and solute movement in the vadose zone and for analyzing specific laboratory and field experiments involving unsaturated water flow and solute transport (Šimůnek and Suarez 1997; Gonçalves et al. 2006; Seaman et al. 2012). Unfortunately, the evaluation of these models under field conditions is still very limited, largely because they need a variety of input data, such as the soil's hydraulic properties, the solute transport parameters, and the parameters characterizing the partition between the solid phase and the soil solution. Šimůnek and Suarez (1997) combined a major ion chemistry module with both one- and two-dimensional variably saturated water flow model, while also considering solute transport, carbon dioxide transport, and heat flow. The UNSATCHEM model considers kinetic chemical reactions, such as the precipitation/dissolution of calcite and the dissolution of dolomite. Because the models can evaluate the activity

coefficients, they can also be used to assess chemical reactions for solutions with very high ionic strengths. The major ion chemistry and carbon dioxide modules of the UNSATCHEM model were later incorporated in the HYDRUS-1D software package (Šimůnek et al. 2012). This model represents a relatively powerful tool for evaluating major ion chemistry in the subsurface by providing quantitative predictions of the amount of water and adjustment required to reclaim sodic and saline soils to the desired levels of salinity and ESP (Šimůnek and Suarez 1997; Ramos et al. 2011).

The objective of this study was to analyze adsorption exchange and dynamic changes of cation in the process of reclaiming sodic soils with CaSO_4 using a multicomponent solute transport equation in which chemical reactions such as cation exchange, precipitation, and dissolution of the soil phase (reclamation amendments) were considered. The effects of the soil saturated hydraulic conductivity (K_s) and electrical conductivity (EC) on reclamation were considered to evaluate the effectiveness of the UNSATCHEM software package in predicting the concentrations of individual ions, electrical conductivity (EC), and SAR under soil column conditions and to provide a theoretical basis for the field application of amendment alternatives (such as BFGD).

Materials and methods

Materials

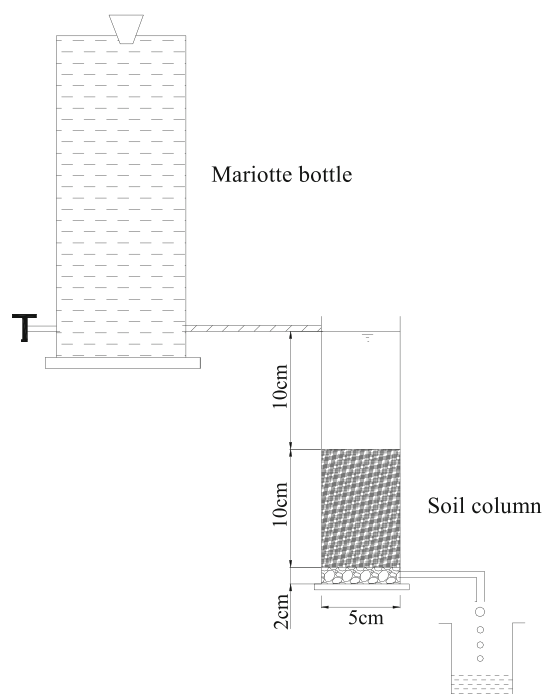
This Ca^{2+} application experiment was carried out in the Soil Physics Laboratory of the China Agricultural University. The purpose of the Ca^{2+} application experiment was to study the variation in Na^+ and Ca^{2+} in the soil leachate, soil solution, and soil colloid during sodic soil reclamation by CaSO_4 . Because BFGD contains CaCO_3 precipitates and impurities, pure CaSO_4 was used as a substitute for BFGD to more precisely examine the mechanism of sodic soil reclamation by BFGD.

The soil was sampled from the Changsheng Experimental Station of the Baoyannur League Institute of Water Resources in northwest China (N40°20', E108°31') using a spade. The soil is Kastanozems and had typical sodic soil characteristics: a high pH and exchangeable sodium percentage and low hydraulic conductivity. The soil texture was clay, and its physical and chemical properties are listed in Table 1. The soil was air-dried, crushed, and passed through a 2-mm sieve before the experiments. Pure CaSO_4 (molecular weight 136) was from the Tianjin Wendaxigui Chemical Reagent Factory.

Table 1 Physical and chemical properties of the soils

Exchangeable cations (cmol _c kg ⁻¹)					Soil bulk density (g cm ⁻³)	pH _{1:5}	
Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	CEC			
8.65	0.60	0.50	1.27	11.02	1.45		9.15
Soluble cations (mmol _c L ⁻¹)				Soluble anions (mmol _c L ⁻¹)			
Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻
303.15	5.18	3.33	3.33	193.33	50.00	51.67	20.00
Particle size distribution (%)			SAR _{1:5}	ESP	EC _{1:5} (dS m ⁻¹)		K _s (cm h ⁻¹)
2.0–0.02	0.02–0.002	<0.002					
23.2	34.7	42.1	166.13	78.49	0.95		0.25

The solution of measured soluble ions, EC, and pH is 1:5 soil to water extracts

**Fig. 1** Experimental Ca²⁺ application device

Methods

The Ca²⁺ application experiment was carried out in the Soil Physics Laboratory of China Agricultural University in August 2005. The experimental device (Fig. 1) was a 25-cm-high plexiglass column with a 5-cm inner diameter (the soil height was 10 cm), and a Mariotte bottle was used to supply water. The experiment consisted of four treatments with different CaSO₄ rates (0.5, 1, 1.5, and 2 g L⁻¹). Pure CaSO₄ was selected as the reagent, and distilled water was used as the solvent to configure the solution.

The tested soil samples were poured homogeneously into the plexiglass column at a dry soil bulk density of

1.45 g cm⁻³ to a depth of 10 cm. The soil columns were saturated with distilled water from the bottom up. Once the soils were saturated, the surface water was quickly drained with a vacuum pump, and the Ca²⁺ solution that had been configured in the Mariotte bottle was immediately supplied. The soil leachate was collected in a graduated cylinder. The volume, pH, EC, and Ca²⁺ and Na⁺ concentrations of the leachate were measured once every 24 h. The Ca²⁺ and Na⁺ concentrations in the soil solution and soil colloid were measured after the application experiment.

Analytical methods and statistical analyses

The soil samples were air-dried and passed through a 1-mm sieve. The EC, pH, soluble anions and soluble cations were measured using 1:5 soil to water extracts. The soluble cations were measured using an atomic absorption spectrophotometer, soluble anions were determined by anion chromatography, the soil pH was determined using the glass electrode method, and the EC was measured using a 1-cm conductivity cell with a dip-type probe. Exchangeable cations were determined in a 1 M ammonium acetate (pH = 7) extract. Following this extraction and washing with 96 % alcohol, the cation exchange capacity was determined by the removal of ammonium ions by distillation. Na⁺ and K⁺ were determined by flame emission spectroscopy in the extract, and Ca²⁺ and Mg²⁺ were determined by atomic absorption spectrophotometry.

The concentrations of Na⁺ and Mg²⁺ in the leachate were measured using an atomic absorption spectrophotometer. The pH of the leachate was determined using the glass electrode method, and the EC of the leachate was measured using a 1-cm conductivity cell with a dip-type probe.

The K_s was determined using a cutting ring and calculated by Darcy's law. The bulk density was obtained by

drying volumetric soil samples at 105 °C. The dispersion coefficient was obtained with the nonlinear parameter estimation code CXTFIT 2.1 of Toride et al. (1995) by fitting analytical solutions of the CDE to observed penetration data.

The SAR of the soil solution was calculated as

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

The chemical analysis was replicated three times. The standard errors of the means of the three samples from each treatment were calculated. The variations between the treatments were analyzed using SAS 9.1 (Statistical Analysis System; SAS Institute Inc.), and P values <0.05 were considered to be significant. In addition to a visual check, measured values of Ca^{2+} and Na^+ were compared with the results of the UNSATCHEM simulations using the mean absolute error and the root mean square error. The mean absolute error (MAE) given by

$$\text{MAE} = \frac{1}{n} \sum_{i=1}^n |X_{mi} - X_{si}|, \quad (2)$$

describes the difference between the measured values (X_{mi}) and simulation results (X_{si}) in the units of a particular variable, with n being the number of measurement of Ca^{2+} and Na^+ . The root mean square error (RMSE) given by

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (X_{mi} - X_{si})^2}{n - 1}}, \quad (3)$$

is the square root of the mean square error, also given in the units of a particular variable. In general, $\text{RMSE} \geq \text{MAE}$. The degree in which the RMSE value exceeds MAE is usually a good indicator of the presence and extent of outliers, or the variance of the differences between the modeled and observed values.

UNSATCHEM software package

UNSATCHEM 2.0 (Šimůnek et al. 1996) was used to simulate the process of sodic soil reclamation by calcium. UNSATCHEM is a software package for simulating one-dimensional variably saturated water flow, heat transport, carbon dioxide production and transport, and multicomponent solute transport with major ion equilibrium and kinetic chemistry.

Saturated water flow movement

Soil water flow movement equation

The one-dimensional movement of water in a saturated rigid porous medium was described by the Richards equation (Richards 1952; Šimůnek and Suarez 1997):

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial z} \left[K_s \left(\frac{\partial h}{\partial z} + 1 \right) \right], \quad (4)$$

where h is the water pressure head in cm, K_s is the initial saturated hydraulic conductivity of the tested soil in cm h^{-1} , t is the leaching time in h, and z is the spatial coordinate (positive upward).

The effect of the solution chemistry on the hydraulic conductivity was implemented as

$$K(h, \text{pH}, \text{SAR}, C_0) = r(\text{pH}, \text{SAR}, C_0) K(h), \quad (5)$$

where SAR is the sodium adsorption ratio, C_0 is the total salt concentration of the ambient solution in $\text{mmol}_e \text{L}^{-1}$, and r is the scaling factor related to the pH, SAR, and salinity.

Initial and boundary conditions

The Ca^{2+} application test followed the saturated infiltration process. In the initial state, the entire soil column was saturated. The movement of water in soil was described as an infiltration process. The upper boundary condition of the soil column has a 10-cm constant water head. The lower boundary was the free-flow boundary, with a 20-cm constant water head.

Multicomponent solute transport

Solute transport equations

The partial differential equation governing one-dimensional advective–dispersive chemical transport under transient water flow conditions in a partially saturated porous medium is as follows (Šimůnek and Suarez 1997; Suarez and Šimůnek 1997):

$$\frac{\partial \theta_w c_k}{\partial t} + \rho \frac{\partial \bar{c}_k}{\partial t} + \rho \frac{\partial \hat{c}_k}{\partial t} = \frac{\partial}{\partial z} \left[\theta_w D \frac{\partial c_k}{\partial z} - q_w c_k \right] \\ k = 1, 2, \dots, N_c, \quad (6)$$

where c_k is the total soluble concentration of the aqueous species k in g cm^{-3} (the values in the initial conditions are shown in Table 1) and $\bar{c}_k$ is the total exchangeable species concentration of the aqueous component k in g g^{-1} ; the values for both of these parameters under the initial conditions are shown in Table 1. $\hat{c}_k$ is the total solid phase concentration of the aqueous component in g g^{-1} . The precipitation of gypsum and calcium carbonate was considered in this study, and the total solid phase concentration of calcium in the initial conditions is 0. ρ is the bulk density of the medium in g cm^{-3} , which is 1.45 g cm^{-3} according to Table 1. D is the dispersion coefficient ($5.60 \text{ cm}^2 \text{ h}^{-1}$ under the initial conditions); q_w is the volumetric flux (0.25 cm h^{-1} under initial conditions); and N_c is the number of primary aqueous species. Eight aqueous species (CO_3^{2-} , HCO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , K^+ and Na^+) were considered in this study.

Cation exchange and selectivity

The partition between the solid phase and the solution was described by the Gapon equation (White and Zelazny 1986):

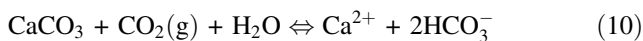
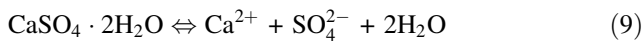
$$K_{ij} = \frac{\bar{c}_i^{y+} (c_j^{x+})^{1/x}}{\bar{c}_j^{x+} (c_i^{y+})^{1/y}}, \quad (7)$$

where y and x are the valence of species i and j , respectively, and K_{ij} is the Gapon selectivity coefficient. The adsorption concentration is expressed in mol kg^{-1} of soil. The cation exchange capacity, $\bar{c}_T(\text{CEC})$, was assumed to be constant and independent of pH:

$$\bar{c}_T = \sum \bar{c}_i = \bar{Ca}^{2+} + \bar{Mg}^{2+} + \bar{Na}^{+} + \bar{K}^{+}. \quad (8)$$

Precipitation dissolution reactions

The precipitation or dissolution of gypsum and calcium carbonate in the presence of CO_2 is described by



with the corresponding solubility products K_{sp} :

$$K_{\text{sp}}^{\text{G}} = (\text{Ca}^{2+})(\text{SO}_4^{2-})(\text{H}_2\text{O})^2 \quad (11)$$

$$K_{\text{sp}}^{\text{C}} = (\text{Ca}^{2+})(\text{CO}_3^{2-}). \quad (12)$$

Initial and boundary conditions

The soil columns were saturated with distilled water from the bottom up. The upper surface water was quickly drained with a vacuum pump, and the Ca^{2+} solution that had been configured in the Mariotte bottle was immediately injected. The concentrations of Ca^{2+} , Na^{+} , K^{+} , Mg^{2+} , Cl^{-} , SO_4^{2-} , HCO_3^{-} , and CO_3^{2-} in the saturated soil solution under the initial conditions were 3.33, 303.15, 5.18, 3.33, 193.33, 50.00, 51.67, and 20.00 $\text{mmol}_c \text{ L}^{-1}$, respectively. The exchangeable cations of Ca^{2+} , Na^{+} , K^{+} and Mg^{2+} in soil colloids under the initial conditions were 0.50, 8.65, 0.60, and 1.27 $\text{cmol}_c \text{ kg}^{-1}$, respectively.

Results

Changes in the physical and chemical properties of the soil and leachate under Ca^{2+} application

pH of the leachate

The changes in the leachate pH under different Ca^{2+} application treatments are shown in Fig. 2. The leachate pH gradually decreased as the leaching time increased in

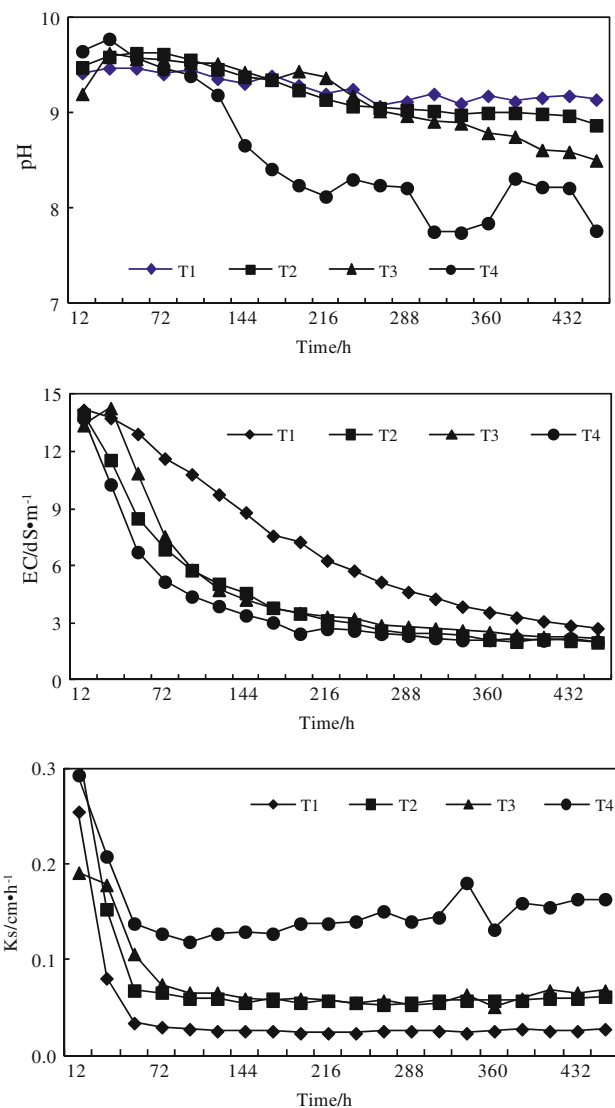


Fig. 2 Changes in the pH, EC, and Ks in soil leachate with leaching time. **a** T1; **b** T2; **c** T3; **d** T4

all of the treatments. The leachate pH decreased as the Ca^{2+} concentration in the supplied water increased. When the Ca^{2+} concentration in the supplied water was $29.41 \text{ mmol}_c \text{ L}^{-1}$, the pH of the leachate was <8.5 after 480 h. The soil solution pH of 8.5 illustrated that the carbonate and bicarbonate had reduced and that the soluble salt had gradually transitioned from sodic to neutral salt.

EC of the leachate

The changes in the EC of the leachate under different treatments are shown in Fig. 2. The EC of the leachate gradually decreased under all four treatments. The changes had two characteristics: (1) when the Ca^{2+} concentration in the supplied water was higher, the decrease in the EC of the leachate was more significant; and (2) the decrease in the

EC was more significant in the initial stage and stabilized thereafter.

Soil hydraulic conductivity

The changes in the hydraulic conductivity of the soil column under different treatments are shown in Fig. 2. The hydraulic conductivity changes exhibited the following trends: (1) the hydraulic conductivity first decreased significantly, then stabilized before gradually increasing; and (2) when the Ca^{2+} concentration in the supplied water was higher, the soil hydraulic conductivity was also higher.

ESP and exchangeable cations in soil colloid

The exchangeable cations and ESP measured at the end of Ca^{2+} application experiment are shown in Fig. 3. The ESP and Na^+ decreased significantly after applying CaSO_4 and leaching in each treatment, and the exchangeable Ca^{2+} markedly increased. When the Ca^{2+} concentration in the supplied water was higher, the extent of increase or decrease was greater.

Changes and simulations of Ca^{2+} and Na^+ concentrations under Ca^{2+} application

Ca^{2+} and Na^+ concentration in the leachate

The measured values and simulation results for the Ca^{2+} concentrations in the leachate are shown in Fig. 4. When the Ca^{2+} concentrations in the supplied water were 14.71, 22.06, and 29.41 mmol L^{-1} , penetration of the Ca^{2+} was realized. When the Ca^{2+} concentration in the supplied water was higher, the Ca^{2+} penetration was faster. Ca^{2+} did not penetrate when the Ca^{2+} concentration was 7.35 mmol L^{-1} . In the initial stage, because the soil solution itself contained a certain amount of soluble Ca^{2+} , the Ca^{2+} in the supplied water first reacted with the sodic salts and exchangeable Na^+ in the soil colloids in the topsoil. Before the Ca^{2+} in the supplied water reached the bottom of the soil column, the Ca^{2+} in the soil solution was

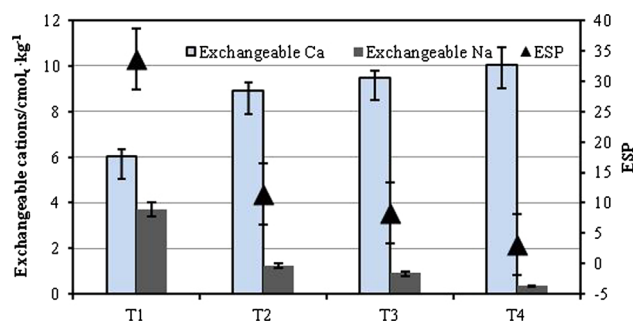


Fig. 3 Exchangeable cations and ESP at the end of the Ca^{2+} application experiment

constantly leached from the soil column, and the Ca^{2+} concentration in the leachate gradually decreased. However, as the Ca^{2+} in supplied water gradually reached the bottom of the soil column, the Ca^{2+} concentration in the leachate gradually increased until it reached the Ca^{2+} concentration in the supplied water, at which point it stabilized.

The measured values and simulation results for the Na^+ concentrations in the leachate are shown in Fig. 5. The Na^+ concentration in the leachate gradually decreased as the concentration of soil Na^+ in the soil solution decreased. Under higher leachate concentrations, the decrease in Na^+ was faster.

The simulation of the Ca^{2+} and Na^+ changes in the leachate during Ca^{2+} application can be conducted by UNSATCHEM. The simulation results and measured values of the Ca^{2+} and Na^+ concentrations in the leachate were generally consistent. In the simulation, the Ca^{2+} in the leachate under different treatments decreased slightly in the initial stage, then slowly increased, and finally rapidly increased. Because the Ca^{2+} in the supplied water was not transported to the bottom of the soil column in the initial stage, the Ca^{2+} in the leachate was the only one contained in the soil solution itself. As Ca^{2+} was constantly transported to the bottom of the soil column, the Ca^{2+} concentration in the leachate increased constantly. However, because the Ca^{2+} in the supplied water reacted with the sodic salts in the soil solution and the Na^+ in the soil colloid, which consumed some of the Ca^{2+} , the increase in the Ca^{2+} concentration in the leachate was not very high. As the Na^+ in the soil colloid was constantly displaced by Ca^{2+} , the Ca^{2+} adsorbed in the soil colloid obtained saturation status, and the displacement reaction stopped. The Ca^{2+} concentration in the leachate quickly increased until it was near that in the supplied water and brought about Ca^{2+} penetration.

The measured values of Na^+ in the leachate and the simulation values in the initial stage (i.e., when the Na^+ concentration in the leachate was higher) were consistent, but in the last stage (i.e., when the Na^+ concentration in the leachate was lower), the measured values were slightly higher than the simulation values. The discrepancy was most likely observed because a portion of the soil solution's becoming stuck in the 5-cm-thick gravel filter layer in the bottom of the soil column such that the Na^+ stranded in the gravel filter layer was slowly diluted and outflowed when the Na^+ concentration was low. Hence, the decrease in the measured Na^+ concentration was slower than that of the simulation value when the Na^+ concentration was low.

Ca^{2+} and Na^+ concentration in soil solution

The simulation results for the Ca^{2+} concentrations in the soil solution using the multicomponent solute transport

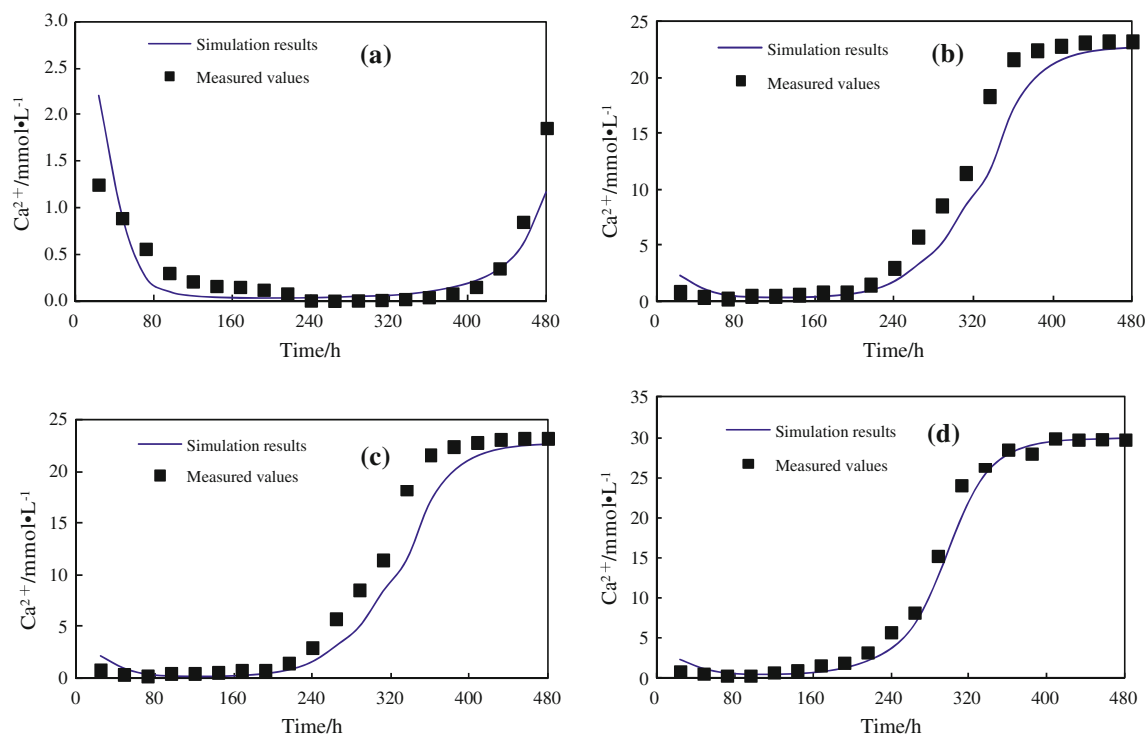


Fig. 4 Change in the measured values and simulation results of Ca^{2+} in the leachate with leaching time. **a** T1; **b** T2; **c** T3; **d** T4

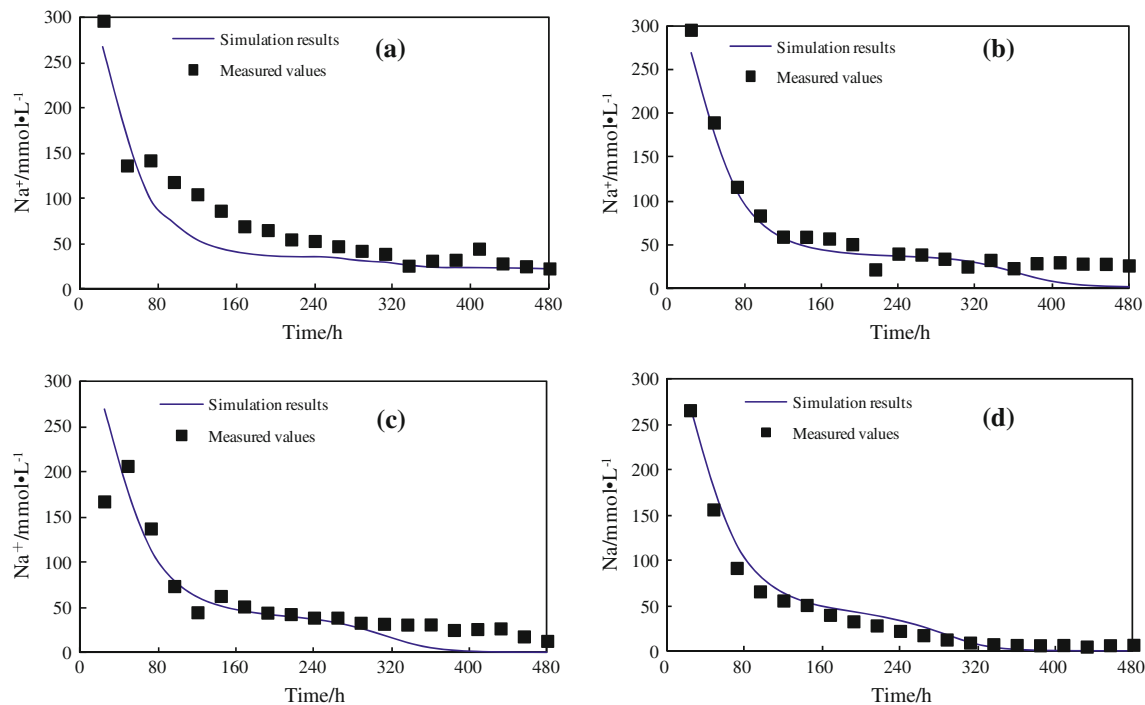
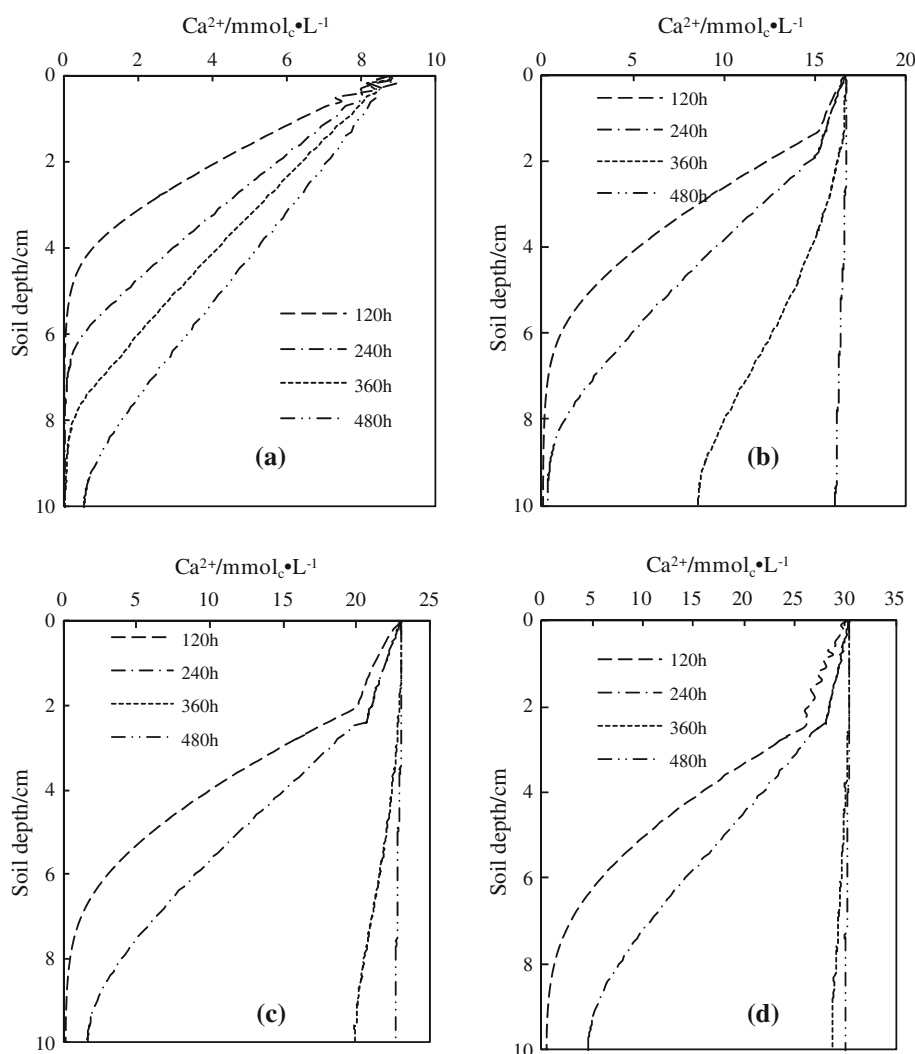


Fig. 5 Change in the measured values and simulation results of Na^{+} in the leachate with leaching time. **a** T1; **b** T2; **c** T3; **d** T4

model are shown in Fig. 6. The Ca^{2+} concentrations simulated by the UNSATCHEM at different soil depths reflected the Ca^{2+} changes in the soil solution. The Ca^{2+} concentration in the soil solutions under different

treatments gradually increased with leaching time. With a higher Ca^{2+} concentration in the supplied water, the magnitude of the Ca^{2+} increase in the soil solution was higher and the increase was faster; hence, the penetration

Fig. 6 Change in the Ca^{2+} concentration in the soil solution with leaching time. **a** T1; **b** T2; **c** T3; **d** T4



time was shorter, and there was a significant increase in the depth of Ca^{2+} . At first, the Ca^{2+} concentration in the soil solution increased quickly in the surface soil, and with the constant transportation of Ca^{2+} from top to bottom, the increase in the Ca^{2+} concentration gradually moved to the bottom of the soil column. Once the Ca^{2+} had penetrated the soil column, the Ca^{2+} concentration reached the maximum value in both the top and bottom soil, which was almost equal to the Ca^{2+} concentration in the supplied water.

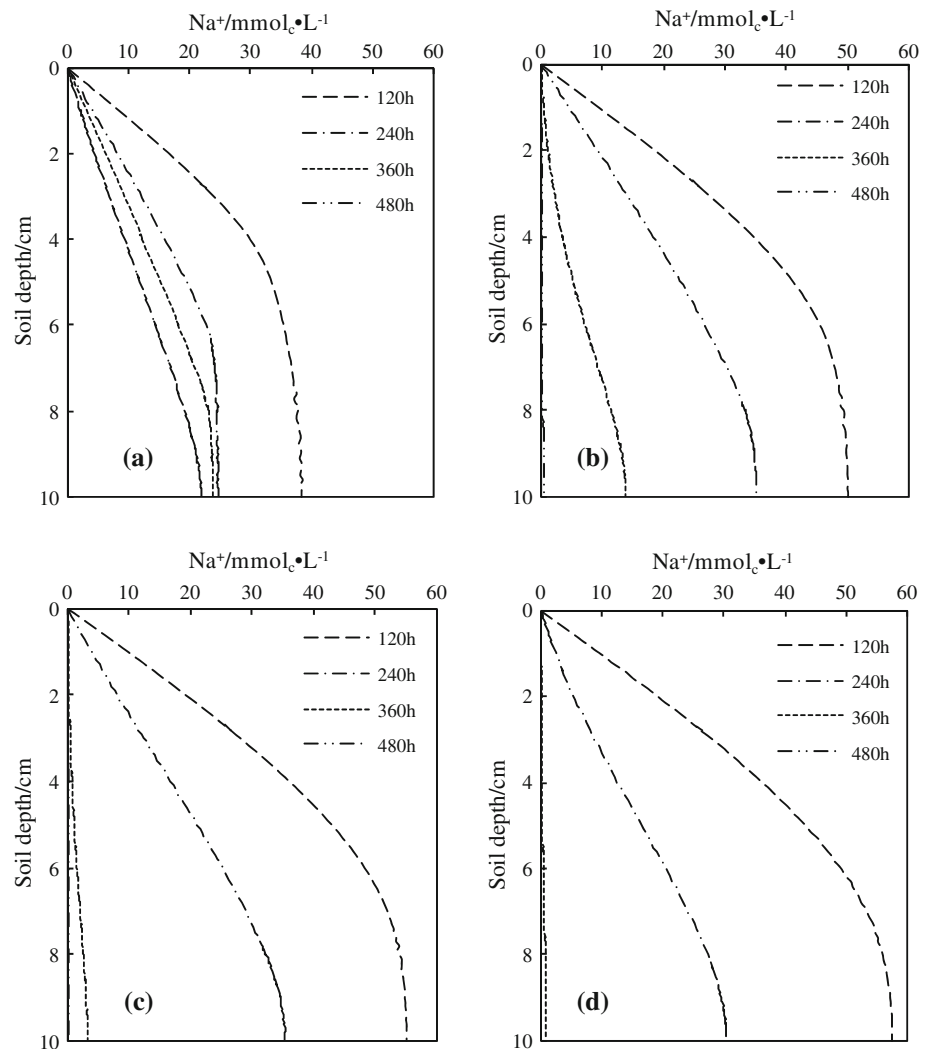
The simulation results for the Na^{+} concentrations in the soil solution using the multicomponent solute transport model are shown in Fig. 7. The Na^{+} concentrations simulated by the UNSATCHEM at different soil depths reflected the Na^{+} changes in the soil solution. The Na^{+} concentration of the soil solution under different treatments gradually decreased as the leaching time increased. When the Ca^{2+} concentration in the supplied water was higher, the magnitude of the decrease in Na^{+} was more significant, because as the leachate concentration increased, the

hydraulic conductivity of the soil also increased, and thus Na^{+} outflow from the soil column accelerated. When the supplied water concentration was higher, the sodic soil reclamation was faster, the physical and chemical properties were better, and the Na^{+} decreased faster. The decrease in the Na^{+} concentration in the soil solution was greater in the topsoil than in the bottom soil, mainly because the Na^{+} in the topsoil had to flow through the bottom soil before it was leached out of the soil, resulting in some accumulation.

Ca^{2+} and Na^{+} concentration in the soil colloid

The simulation results of the Ca^{2+} concentration in the soil colloid using the multicomponent solute transport model are shown in Fig. 8. The Ca^{2+} concentrations simulated by the UNSATCHEM at different soil depths better reflect the Ca^{2+} changes in the soil colloid. As the leaching time increased, the Ca^{2+} concentration at each depth gradually increased under different treatments, and the magnitude of

Fig. 7 Change in the Na^+ concentration in the soil solution with leaching time. **a** T1; **b** T2; **c** T3; **d** T4



the increase in exchangeable Ca^{2+} in the surface soil was more significant than that in the topsoil. As the Ca^{2+} concentration in the supplied water increased, the magnitude of the increase in exchangeable Ca^{2+} also increased. At first, the Ca^{2+} concentration in the soil colloid quickly increased in the surface soil, and the Na^+ in the soil colloid was continuously replaced by the Ca^{2+} in the supplied water. Once the Ca^{2+} saturated the surface soil colloid, it was gradually transported to the lower part of the soil column. Once Ca^{2+} infiltrated the soil column, Ca^{2+} in the soil colloid was at the maximum at the surface and bottom of the soil column.

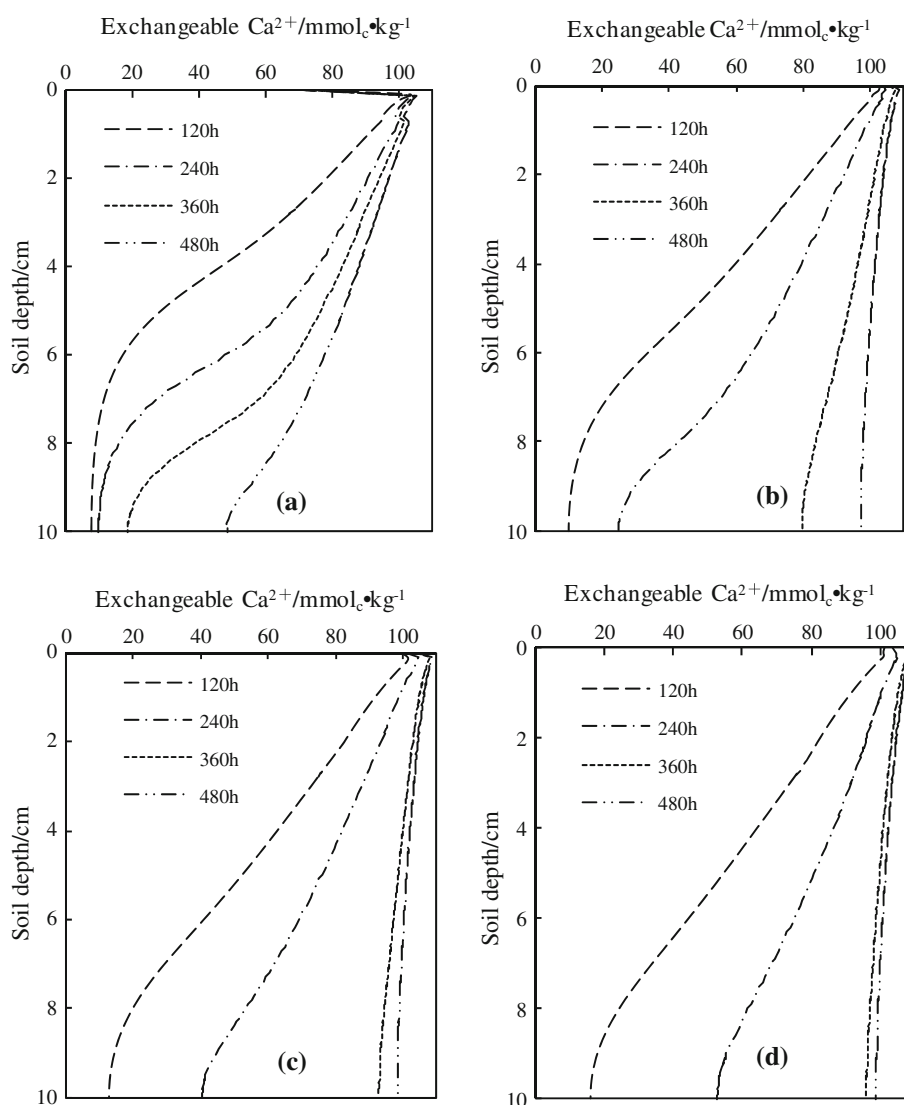
The simulation results for the Na^+ concentrations in the soil colloid using the multicomponent solute transport model are shown in Fig. 9. The Na^+ concentrations simulated by the UNSATCHEM at different soil depths can better reflect the changes in Na^+ in the soil colloid. The change in the Na^+ concentration in the soil colloid was opposite to the change in Ca^{2+} . The $\overline{\text{Na}^+}$ in the soil colloid

gradually decreased with the increase in leaching time under the different treatments, and the magnitude of the decrease in $\overline{\text{Na}^+}$ in the surface soil was more significant than that in the topsoil. The magnitude of the decrease in $\overline{\text{Na}^+}$ was greater for higher Ca^{2+} concentration, mainly due to the speed at which the Ca^{2+} in the soil solution replaced Na^+ in the soil colloid as the Ca^{2+} concentration in the soil solution increased. The physical and chemical properties of the soil also improved.

Amount of CaSO_4 precipitation

The simulation results for CaSO_4 precipitation at different soil depths using the multicomponent solute transport model are shown in Fig. 10. For those treatments in which the Ca^{2+} concentrations in the supplied water were 14.71, 22.06, and 29.41 mmol L^{-1} , CaSO_4 precipitation occurred in 0-2 cm of the surface soil. As the Ca^{2+} and SO_4^{2-} concentrations in the supplied water increased, the depth

Fig. 8 Changes in the exchangeable Ca^{2+} concentration in the soil colloid with leaching time. **a** T1; **b** T2; **c** T3; **d** T4



and weight of CaSO_4 precipitation increased because all of the Ca^{2+} was saturated in the surface soil solution and the soil colloid and the solubility of CaSO_4 were very low (2 g L^{-1}). CaSO_4 cannot precipitate in the topsoil with the inflow of Ca^{2+} and SO_4^{2-} . When the Ca^{2+} concentration in the supplied water was 7.35 mmol L^{-1} , it was far less than the CaSO_4 precipitation.

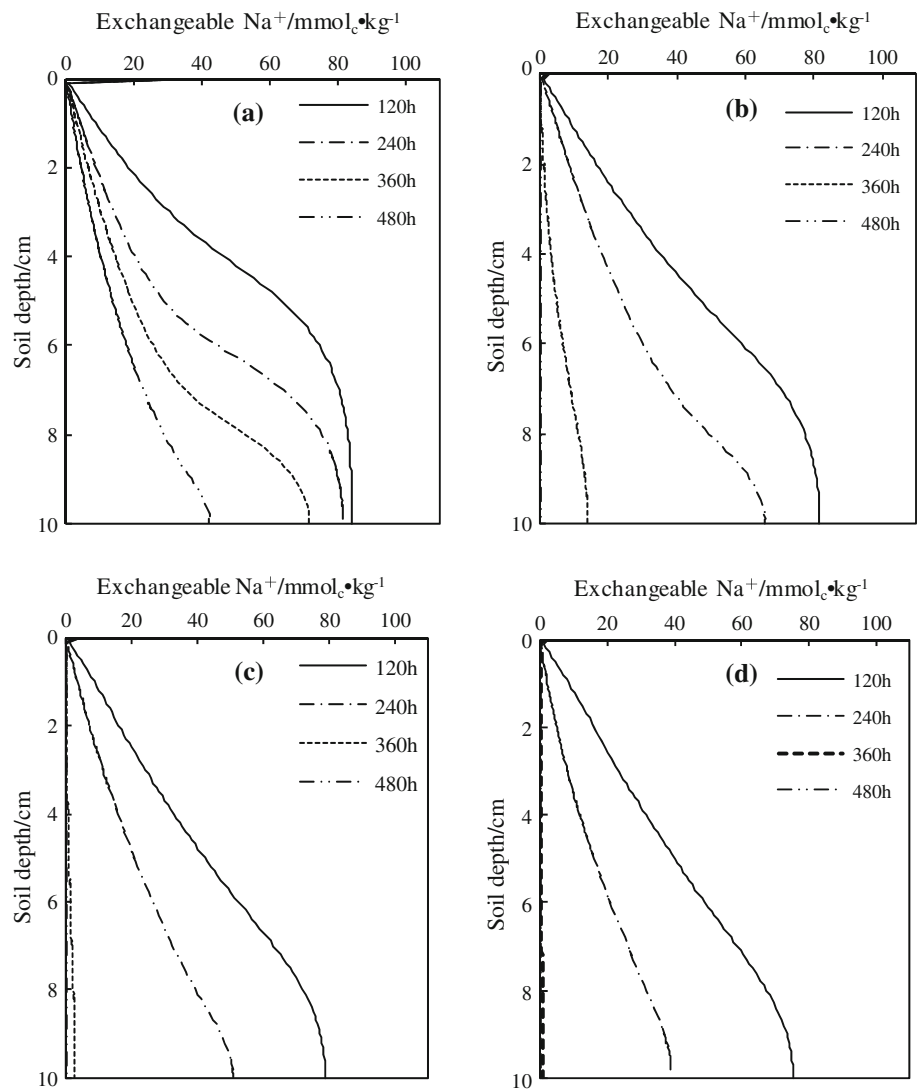
Discussion

Feasibility of the UNSATCHEM simulation

The UNSATCHEM model with the major ion chemistry module used in this study has a relatively complex code and requires a large number of input parameters that are not always readily available (Šimůnek et al. 2012; Kanzari

et al. 2012). In this study, precipitation dissolution and adsorption exchange were considered (Visconti et al. 2012). The obtained adsorption exchange coefficients were 1.91 for $K_{\text{Ca-Na}}$, 0.82 for $K_{\text{Ca-Mg}}$, and 1.08 for $K_{\text{Ca-K}}$ according to the initial soluble and adsorbed cation concentrations. Note that the Ca^{2+} and Na^{+} concentrations simulated by the UNSATCHEM at different soil depths reflect the measured values. The RMSE between the measured values and simulation results of Ca^{2+} in leachate were 0.29, 1.90, 2.34, and 1.40 mmol L^{-1} with CaSO_4 concentrations of 0.5, 1, 1.5, and 2 g L^{-1} , respectively, and 26.10, 15.70, 28.43 and $10.87 \text{ mmol L}^{-1}$ for Na^{+} in leachate, respectively. All the RMSE of the UNSATCHEM simulations were less than MAE in different degrees, and the use of the multicomponent solute transport model for the numerical simulation of multicomponent solute transport in sodic soils reclaimed by CaSO_4 was reasonable.

Fig. 9 Changes in the exchangeable Na^+ concentration in the soil colloid with leaching time. **a** T1; **b** T2; **c** T3; **d** T4

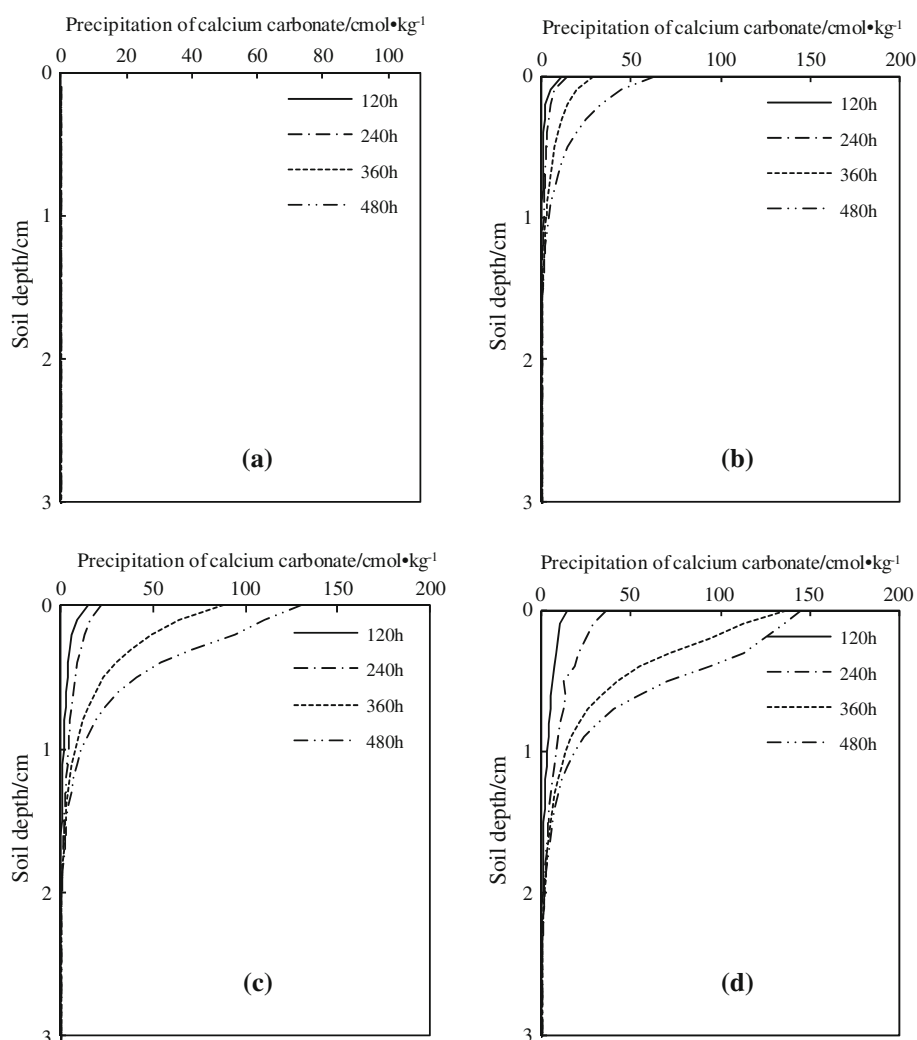


Function of Ca^{2+} in sodic soil reclaimed by CaSO_4

The Ca^{2+} concentration in the soil solution increased with the dissolution of CaSO_4 . Thus, the proportion of Na^+ in soil solution composition and the SAR of the soil solution decreased. This change contributed to the flocculation of clay soil and the improvement of hydraulic conductivity properties. K_s is an important parameter in the expression of soil hydraulic characteristics and is related to the cation composition and content in the irrigation water and soil solution and the soluble electrolyte concentration (USDA 1954; McNeal 1968; Basile et al. 2012). The K_s increases as the Ca^{2+} concentration of the soil solution increases (David and Dimitrios 2002; USDA 1954; Gill et al. 2008). Therefore, when the Ca^{2+} concentration in the supplied water was high, the soil hydraulic conductivity properties were better than those of low Ca^{2+} concentration. At the same time, because the soil contained some salts in the

initial stage, the EC decreased significantly as the salts were constantly leached from the soil column. With the decrease in the salt content in the soil, the soil EC of the leachate gradually stabilized. In the saturated soil, K_s is not constant; rather, it changes with the cation composition in the soil solution (Reading et al. 2012). In this study, K_s was regarded as dynamically changing; it increased as the soil solution concentration increased and was, therefore, superior under the treatment with a higher Ca^{2+} concentration. In addition, the amount of soil leachate was also higher. In the initial stage, the physical and chemical properties were good, and the K_s was high. However, with the continuous dispersion and swelling of the soil clay, the soil's physical properties continuously deteriorated. At the same time, the soil porosity decreased constantly under the action of water pressure, and the soil hydraulic conductivity gradually decreased. With continuous supplementation of Ca^{2+} , an ion adsorption exchange reaction occurred, the soil's

Fig. 10 Change in the precipitation of calcium carbonate with leaching time. **a** T1; **b** T2; **c** T3; **d** T4



physical properties continuously improved, and Ks slowly increased. The higher the Ca²⁺ concentration in the supplied water, the more obvious the improvement.

Conclusions

The ion adsorption exchange mechanism of sodic soil reclaimed by CaSO₄ was analyzed in an ion application experiment, and the UNSATCHEM was used to simulate ion adsorption exchange process. The following conclusions can be drawn from our findings.

1. The Ca²⁺ achieved penetration when the Ca²⁺ concentrations in the supplied water were 14.71, 22.06, and 29.41 mmol L⁻¹, but not 7.35 mmol L⁻¹. The time taken to achieve penetration decreased as the Ca²⁺ concentration in the supplied water increased.
2. The UNSATCHEM was able to accurately simulate the transportation and transformation of Ca²⁺ and

Na⁺ in the soil solution during Ca²⁺ application, the adsorption and exchange between Na⁺ in the soil colloid and Ca²⁺ in the soil solution, and the precipitation and dissolution of CaSO₄.

3. The process of reclaiming sodic soils by calcium sulfate was complex and considered by ion adsorption exchange and precipitation dissolution reactions and was also affected by the soil's physical and chemical properties. The process was notably lengthy and could be improved. First, leaching should be supplemented by constantly applying dissolved BFGD to the surface and later adding it to the bottom soil. Second, applying the CaSO₄ in batches helps the sodic soil maintain a certain Ca²⁺ content over a longer period, thereby providing sustained improvements.

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