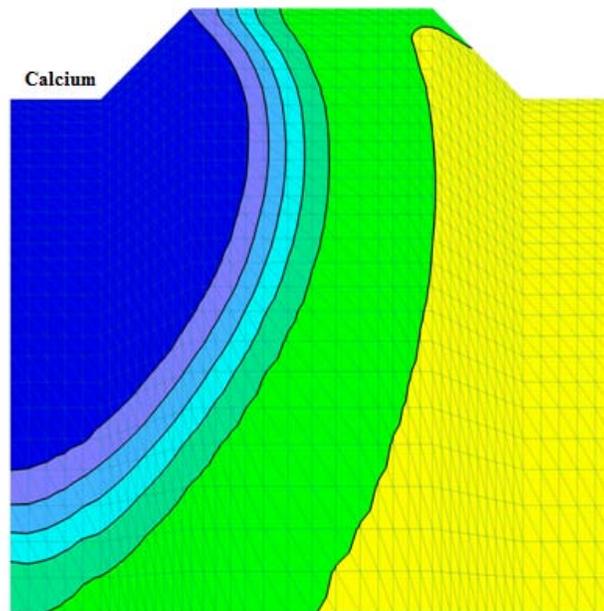


The UNSATCHEM Module

for HYDRUS (2D/3D)

Simulating Two-Dimensional Movement of
and Reactions Between Major Ions in Soils

Version 1



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Abstract

Šimůnek, J., M. Šejna, and M. Th. van Genuchten, The UNSATCHEM Module for HYDRUS (2D/3D) Simulating Two-Dimensional Movement of and Reactions Between Major Ions in Soils, Version 1.0, PC Progress, Prague, Czech Republic, 52 pp., 2012.

This report documents the geochemical **UNSATCHEM** module [Šimůnek and Suarez, 1994; Šimůnek *et al.*, 1996] that has been implemented into the two-dimensional computational module of the **HYDRUS (2D/3D)** software package. The geochemical UNSATCHEM module simulates the transport of major ions in variably-saturated porous media, including major ion equilibrium and kinetic non-equilibrium chemistry. The resulting code is intended for predictions of major ion chemistry, along with water and solute fluxes in soils during transient flow. The major variables of the chemical system in UNSATCHEM are Ca, Mg, Na, K, SO₄, Cl, NO₃, H₄SiO₄, alkalinity, and CO₂. The model accounts for various equilibrium chemical reactions between these components, such as complexation, cation exchange and precipitation-dissolution. For the precipitation-dissolution of calcite and dissolution of dolomite, either equilibrium or multicomponent kinetic expressions can be used, which includes both forward and back reactions. Other dissolution-precipitation reactions considered include gypsum, hydromagnesite, nesquehonite, and sepiolite. Since the ionic strength of soil solutions can vary considerably in time and space and often reach high values, both the modified Debye-Hückel and the Pitzer expressions are incorporated into the model to calculate single ion activities. The effect of solution chemistry on the hydraulic conductivity is also considered. Water flow and heat transport modules are similar (almost identical) as in regular HYDRUS. Applications of the UNSATCHEM module are demonstrated on several examples.

This report serves as both a **Technical** and **User Manual** and is a reference document of the **Graphical User Interface** of the **UNSATCHEM** related parts of the **HYDRUS** software package.

DISCLAIMER

This report documents the UNSATCHEM module of HYDRUS (2D/3D). The UNSATCHEM module was developed as a supplemental module of the HYDRUS software package, to model the transport and reactions of major ions in the soil. The software has been verified against selected test cases. However, no warranty is given that the program is completely error-free. If you do encounter problems with the code, find errors, or have suggestions for improvement, please contact one of the authors at

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1. Introduction

The main purpose of this report is to document the **UNSATCHEM** module [Šimůnek and Suarez, 1994; Šimůnek *et al.*, 1996] of the HYDRUS (2D/3D) software package [Šimůnek *et al.*, 2011; Šejna *et al.*, 2011] for simulating two-dimensional multicomponent transport and reactions of major ions. The two-dimensional variably-saturated water flow and heat movement are described in the HYDRUS (2D/3D) documentation, and will not be repeated here. The UNSATCHEM module is fully supported by the HYDRUS (2D/3D) graphical user interface [Šejna *et al.*, 2011].

The resulting coupled program numerically solves the Richards equation for saturated-unsaturated water flow and convection-dispersion type equations for heat and solute transport. The water flow equation incorporates a sink term to account for water uptake by plant roots. The heat transport equation considers movement by conduction as well as convection with flowing water. The major variables of the chemical system are Ca, Mg, Na, K, SO₄, Cl, NO₃, H₄SiO₄, alkalinity, and CO₂. The model accounts for equilibrium chemical reactions between these components such as complexation, cation exchange and precipitation-dissolution. For the precipitation-dissolution of calcite and dissolution of dolomite, either equilibrium or multicomponent kinetic expressions are used which include both forward and back reactions. Other dissolution-precipitation reactions considered include gypsum, hydromagnesite, nesquehonite, and sepiolite. Since the ionic strength of soil solutions can vary considerably with time and space and often reach high values, both modified Debye-Hückel and Pitzer expressions were incorporated into the model to calculate single ion activities.

The **UNSATCHEM** module may be used to analyze water and solute movement in unsaturated, partially saturated, or fully saturated porous media. **UNSATCHEM** can handle flow domains delineated by irregular boundaries. The flow region itself may be composed of nonuniform soils having an arbitrary degree of local anisotropy. Flow and transport can occur in the vertical plane, the horizontal plane, or in a three-dimensional region exhibiting radial symmetry about a vertical axis. The water flow part of the model considers prescribed head and flux boundaries, as well as boundaries controlled by atmospheric conditions.

The governing flow and transport equations are solved numerically using standard Galerkin-type linear finite element schemes. Applications of the UNSATCHEM module are demonstrated on several examples.

2. Multicomponent Solute Transport

The partial differential equation governing two-dimensional advective-dispersive chemical transport under transient water flow conditions in a partially saturated porous medium is taken as

$$\frac{\partial \theta c_k}{\partial t} + \rho \frac{\partial \bar{c}_k}{\partial t} + \rho \frac{\partial \hat{c}_k}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial c_k}{\partial x_j} \right) - \frac{\partial q_i c_k}{\partial x_i} \quad k = 1, 2, \dots, N_c \quad (2.1)$$

where c_k is the total dissolved concentration of the aqueous component k [ML^{-3}], \bar{c}_k is the total sorbed concentration of the aqueous component k [MM^{-1}], \hat{c}_k is the total concentration of aqueous component k in the minerals, which can precipitate or dissolve [MM^{-1}], ρ is the bulk density of the medium [ML^{-3}], D_{ij} is the dispersion coefficient tensor [L^2T^{-1}], q_i is the volumetric flux [LT^{-1}] and N_c is the number of aqueous components. Solute uptake by plant roots is not considered in (2.1). The second and third terms on the left side of eq. (2.1) are zero for components that do not undergo ion exchange or precipitation/dissolution.

Dispersion coefficients, and initial and boundary conditions are similar as for solute transport in the standard module of HYDRUS (2D/3D).

3. Carbonate Chemistry

3.1. Principles

The carbonate chemistry module was adopted from the UNSATCHEM software package [Šimůnek *et al.*, 1996], and thus their description closely mirrors material in the UNSATCHEM manual. Additional details can be found in the original manual [Šimůnek *et al.*, 1996].

When using the ion-association model (and Debye-Hückel activity coefficient calculations) we assume that the chemical system for predicting major ion solute chemistry of the unsaturated zone includes 37 chemical species. These species are divided into six groups as listed in Table 3.1. They include 7 primary dissolved species (calcium, magnesium, sodium, potassium, sulfate, chloride, and nitrate), 10 complex aqueous species, 6 possible solid phases (calcite, gypsum, nesquehonite, hydromagnesite, sepiolite and dolomite), 4 surface species, 7 species which form the CO₂-H₂O system, and 3 silica species. The species from the last two groups could have been included also in other groups (e.g., CO₃²⁻, H₂SiO₄²⁻, and H⁺ could be included in the first group). Their consideration into separate groups is mainly due to their different treatment compared to the other species. For example, complex species of these groups are considered also at high ionic strength when the Pitzer equations are used to calculate activity coefficients, while the species of the second group are in that case dropped from the system, as discussed later. One of the solid phases (dolomite) is not included in the equilibrium system since its dissolution is always treated kinetically. Also, exclusion of calcite from the equilibrium system is optional since its precipitation-dissolution can be treated as a kinetic process. As a result, either 36 or 35 independent equations are needed to solve this system. In the following sections we present this set of equations, while the method of solution is discussed in Šimůnek *et al.* [1996].

Table 3.1. Chemical species considered in the carbonate chemistry module.

1	Aqueous components	7	Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺ , SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻
2	Complexed species	10	CaCO ₃ ⁰ , CaHCO ₃ ⁺ , CaSO ₄ ⁰ , MgCO ₃ ⁰ , MgHCO ₃ ⁺ , MgSO ₄ ⁰ , NaCO ₃ ⁻ , NaHCO ₃ ⁰ , NaSO ₄ ⁻ , KSO ₄ ⁻
3	Precipitated species	6	CaCO ₃ , CaSO ₄ · 2H ₂ O, MgCO ₃ · 3H ₂ O, Mg ₅ (CO ₃) ₄ (OH) ₂ · 4H ₂ O, Mg ₂ Si ₃ O _{7.5} (OH) · 3H ₂ O, CaMg(CO ₃) ₂
4	Sorbed species	4	Ca, Mg, Na, K
5	CO ₂ -H ₂ O species	7	P _{CO2} , H ₂ CO ₃ [*] , CO ₃ ²⁻ , HCO ₃ ⁻ , H ⁺ , OH ⁻ , H ₂ O
6	Silica species	3	H ₄ SiO ₄ , H ₃ SiO ₄ ⁻ , H ₂ SiO ₄ ²⁻

3.2. Mass and Charge Balance Equations

Seven mass balance equations for the primary species in the 1st group and one for the silica species in the 6th group of Table 3.1 are defined:

$$\begin{aligned}
 \text{Ca}_T &= [\text{Ca}^{2+}] + [\text{CaSO}_4^0] + [\text{CaCO}_3^0] + [\text{CaHCO}_3^+] \\
 \text{Mg}_T &= [\text{Mg}^{2+}] + [\text{MgSO}_4^0] + [\text{MgCO}_3^0] + [\text{MgHCO}_3^+] \\
 \text{Na}_T &= [\text{Na}^+] + [\text{NaSO}_4^-] + [\text{NaCO}_3^-] + [\text{NaHCO}_3^0] \\
 \text{K}_T &= [\text{K}^+] + [\text{KSO}_4^-] \\
 \text{SO}_{4T} &= [\text{SO}_4^{2-}] + [\text{CaSO}_4^0] + [\text{MgSO}_4^0] + [\text{NaSO}_4^-] + [\text{KSO}_4^-] \\
 \text{Cl}_T &= [\text{Cl}^-] \\
 \text{NO}_{3T} &= [\text{NO}_3^-] \\
 \text{SiO}_{4T} &= [\text{H}_4\text{SiO}_4] + [\text{H}_3\text{SiO}_4^-] + [\text{H}_2\text{SiO}_4^{2-}]
 \end{aligned} \tag{3.1}$$

in which variables with subscript *T* represent the total analytical concentration in solution of that particular species, and where brackets refer to molalities (mol kg⁻¹). Two mass balance equations for the total analytical concentration of carbonate and bicarbonate are defined as follows

$$\begin{aligned}
 \text{CO}_{3T} &= [\text{CO}_3^{2-}] + [\text{CaCO}_3^0] + [\text{MgCO}_3^0] + [\text{NaCO}_3^-] \\
 \text{HCO}_{3T} &= [\text{HCO}_3^-] + [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+] + [\text{NaHCO}_3^0]
 \end{aligned} \tag{3.2}$$

which are used to calculate inorganic alkalinity, *Alk* (mol_ckg⁻¹):

$$\text{Alk} = 2\text{CO}_{3T} + \text{HCO}_{3T} + [\text{OH}^-] - [\text{H}^+] \tag{3.3}$$

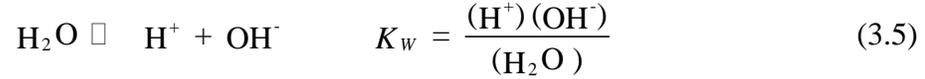
Most chemical and multicomponent transport models consider the total inorganic carbon to be a conservative property [e.g., *Westal et al.*, 1986; *Liu and Narasimhan*, 1989; *Yeh and Tripathi*, 1991]. However, this approach can be used only for closed systems. In a soil profile with fluctuating CO₂ concentrations, the approach is inappropriate and use of alkalinity as a conservative property is preferable.

In addition to the mass balance equations, the overall charge balance equation for the solution is given as

$$\begin{aligned}
 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+] + [\text{H}^+] - 2[\text{CO}_3^{2-}] - \\
 -[\text{HCO}_3^-] - 2[\text{SO}_4^{2-}] - [\text{Cl}^-] - [\text{NO}_3^-] - [\text{OH}^-] - [\text{NaCO}_3^-] - [\text{NaSO}_4^-] - [\text{KSO}_4^-] = 0
 \end{aligned} \tag{3.4}$$

3.3. CO₂ - H₂O System

The activities of the species present in solution at equilibrium are related by the mass-action equations. The dissociation of water is written as follows



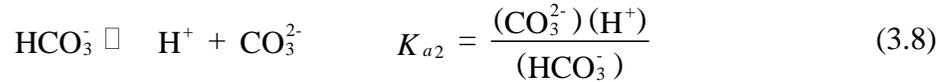
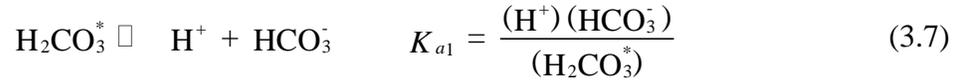
where K_w is the dissociation constant for water [-], while the parentheses denote ion activities. Methods for calculating ion activities will be discussed later.

The solubility of CO₂(g) in water is described with Henry's Law:



where the activity of CO₂(g) is expressed in terms of the partial pressure P_{CO_2} (atm), K_{CO_2} is Henry's law constant and H₂CO₃^{*} represents both aqueous CO₂ and H₂CO₃.

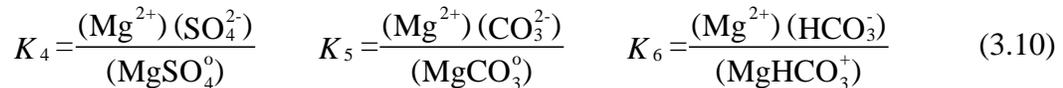
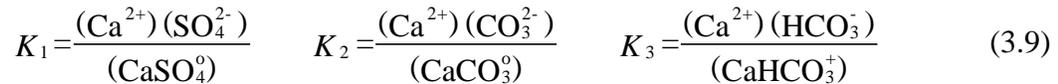
Protolysis reactions of dissolved CO₂ are written as



where K_{a1} and K_{a2} are the first and the second dissociation constants of carbonic acid [-], respectively.

3.4. Complexation Reactions

Each complexation reaction for the species in the second group of Table 3.1 and for the silica species can be represented by a mass action law:



$$K_7 = \frac{(\text{Na}^+)(\text{SO}_4^{2-})}{(\text{NaSO}_4^-)} \quad K_8 = \frac{(\text{Na}^+)(\text{CO}_3^{2-})}{(\text{NaCO}_3^-)} \quad K_9 = \frac{(\text{Na}^+)(\text{HCO}_3^-)}{(\text{NaHCO}_3^0)} \quad (3.11)$$

$$K_{10} = \frac{(\text{K}^+)(\text{SO}_4^{2-})}{(\text{KSO}_4^-)} \quad (3.12)$$

$$K_{11} = \frac{(\text{H}^+)(\text{H}_3\text{SiO}_4^-)}{(\text{H}_4\text{SiO}_4)} \quad K_{12} = \frac{(\text{H}^+)^2(\text{H}_2\text{SiO}_4^{2-})}{(\text{H}_4\text{SiO}_4)} \quad (3.13)$$

where K_i are the equilibrium constants of the i th complexed species [-].

3.5. Cation Exchange and Selectivity

Partitioning between the solid and solution phases is described with the Gapon equation [White and Zelazny, 1986]

$$K_{ij} = \frac{c_i^{-y+} (c_j^{x+})^{1/x}}{c_j^{-x+} (c_i^{y+})^{1/y}} \quad (3.14)$$

where y and x are the valences of species i and j , respectively, and K_{ij} is the Gapon selectivity coefficient [-]. The adsorbed concentration is expressed in ($\text{mol}_c\text{kg}^{-1}$ soil). It is assumed that the cation exchange capacity c_T ($\text{mol}_c\text{kg}^{-1}$ soil) is constant and independent of pH .

$$\bar{c}_T = \Sigma \bar{c}_i \quad (3.15)$$

When four cations ($\bar{\text{Ca}}$, $\bar{\text{Mg}}$, $\bar{\text{Na}}$ and $\bar{\text{K}}$) are involved in the exchange reactions, the following system of equations results:

$$\bar{c}_T = \bar{\text{Ca}}^{2+} + \bar{\text{Mg}}^{2+} + \bar{\text{Na}}^+ + \bar{\text{K}}^+ \quad (3.16)$$

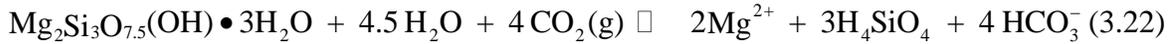
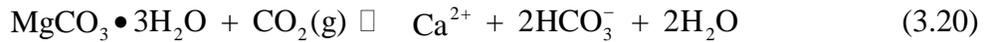
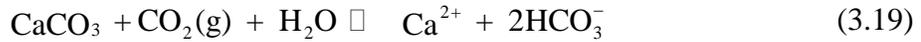
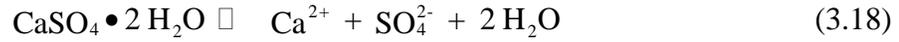
$$K_{13} = \frac{\bar{\text{Mg}}^{2+} (\text{Ca}^{2+})^{1/2}}{\bar{\text{Ca}}^{2+} (\text{Mg}^{2+})^{1/2}}$$

$$K_{14} = \frac{\bar{\text{Ca}}^{2+} (\text{Na}^+)}{\bar{\text{Na}}^+ (\text{Ca}^{2+})^{1/2}} \quad (3.17)$$

$$K_{15} = \frac{\bar{\text{Ca}}^{2+} (\text{K}^+)}{\bar{\text{K}}^+ (\text{Ca}^{2+})^{1/2}}$$

3.6. Precipitation-Dissolution Reactions

The carbonate chemistry module considers four solid phases which, if specified or approached from oversaturation, must be in equilibrium with the solution: gypsum, nesquehonite, hydromagnesite and sepiolite. Precipitation-dissolution of calcite can be optionally treated assuming either equilibrium or by means of rate equations. In the latter case the equation corresponding to calcite equilibrium presented in this section is omitted from the equilibrium system and the rate of calcite precipitation-dissolution is calculated from the rate equation as described later. Dissolution of dolomite, which will also be discussed later, is always considered as a kinetic process and never included in an equilibrium system since ordered dolomite almost never precipitates in soils. We refer to *Suarez and Šimůnek* [1997] for a detailed discussion on how to select and consider these solids. The precipitation or dissolution of gypsum, calcite (if considered in the equilibrium system), nesquehonite, hydromagnesite and sepiolite in the presence of CO₂ are described by



with the corresponding solubility products K_{SP} [-] given by

$$K_{SP}^G = (\text{Ca}^{2+})(\text{SO}_4^{2-})(\text{H}_2\text{O})^2 \quad (3.23)$$

$$K_{SP}^C = (\text{Ca}^{2+})(\text{CO}_3^{2-}) \quad (3.24)$$

$$K_{SP}^N = (\text{Mg}^{2+})(\text{CO}_3^{2-})(\text{H}_2\text{O})^3 \quad (3.25)$$

$$K_{SP}^H = (\text{Mg}^{2+})^5 (\text{CO}_3^{2-})^4 (\text{OH}^-)^2 (\text{H}_2\text{O})^4 \quad (3.26)$$

$$K_{SP}^S = \frac{(\text{Mg}^{2+})^2 (\text{H}_4\text{SiO}_4)^3 (\text{OH}^-)^4}{(\text{H}_2\text{O})^{4.5}} \quad (3.27)$$

where the indexes G , C , N , H , and S refer to gypsum, calcite, nesquehonite, hydromagnesite and sepiolite, respectively.

Substituting (3.5) through (3.8) into (3.23) through (3.27) gives the solubility products for the carbonate solids expressed in terms of bicarbonate, which is almost always the major carbonate ion for conditions ($6 < pH < 10.5$) in which the carbonate chemistry module is assumed to be applicable:

$$(\text{Ca}^{2+})(\text{HCO}_3^-)^2 = K_{SP}^C \frac{K_{CO_2} K_{a1} P_{CO_2} (\text{H}_2\text{O})}{K_{a2}} \quad (3.28)$$

$$(\text{Mg}^{2+})(\text{HCO}_3^-)^2 = K_{SP}^N \frac{K_{CO_2} K_{a1} P_{CO_2}}{K_{a2} (\text{H}_2\text{O})^2} \quad (3.29)$$

$$(\text{Mg}^{2+})^5 (\text{HCO}_3^-)^{10} = K_{SP}^H \frac{K_{CO_2}^6 K_{a1}^6 P_{CO_2}^6}{K_{a2}^4 K_w^2} \quad (3.30)$$

$$(\text{Mg}^{2+})^2 (\text{HCO}_3^-)^4 = K_{SP}^S \frac{K_{CO_2}^4 K_{a1}^4 P_{CO_2}^4 (\text{H}_2\text{O})^{4.5}}{K_w^4 (\text{H}_4\text{SiO}_4)^3} \quad (3.31)$$

Expressing the solubility products in this way significantly decreases the number of numerical iterations necessary to reach equilibrium as compared to when equations (3.23) through (3.27) are used.

3.7. Kinetic Model for Calcite Precipitation-Dissolution

The reaction rates of calcite precipitation-dissolution in the absence of inhibitors such as "foreign ions" and dissolved organic matter, R^C ($\text{mmol cm}^{-2}\text{s}^{-1}$), were calculated with the rate equation of *Plummer et al.* [1978]

$$R^C = k_1 (\text{H}^+) + k_2 (\text{H}_2\text{CO}_3^*) + k_3 (\text{H}_2\text{O}) - k_4 \frac{K_{a2}}{K_{SP}^C} (\text{Ca}^{2+})(\text{HCO}_3^-) \quad (3.32)$$

where

$$k_4 = k_1 + \frac{1}{(\text{H}_S^+)} [k_2 (\text{H}_2\text{CO}_3^*) + k_3 (\text{H}_2\text{O})] \quad (3.33)$$

and where k_1 , k_2 , and k_3 are temperature-dependent first-order rate constants representing the forward reactions ($\text{mmol cm}^{-2}\text{s}^{-1}$), and k_4 is a function dependent on both temperature and CO_2 concentration representing the back reactions ($\text{mmol cm}^{-2}\text{s}^{-1}$). The precipitation-dissolution rate R^C is expressed in mmol of calcite per cm^2 of surface area per second. The term (H_S^+) is the H^+ activity at the calcite surface. Its value is assumed to be (H^+) at calcite saturation where activities of H_2CO_3^* and H_2O at the calcite surface are equal to their bulk fluid values [*Plummer et al.*, 1978]. The temperature dependency of the constants k_1 , k_2 , k_3 is expressed as

$$\log k = a_1 + \frac{a_2}{T} \quad (3.34)$$

where values of the empirical constants a_1 and a_2 are given by *Plummer et al.* [1978]. For conditions where $pH > 8$ and $pCO_2 < 1000$ Pa, an alternative expression for the precipitation rate is used, which is considered more accurate for those conditions [*Inskip and Bloom*, 1985]

$$R^C = -11.82[(Ca^{2+})(CO_3^{2-}) - K_{sp}^C] \quad (3.35)$$

with an apparent Arrhenius activation energy of 48.1 kJ mol⁻¹ for the precipitation rate constant [*Inskip and Bloom*, 1985].

The precipitation or dissolution rate of calcite is reduced by the presence of various inhibitors. *Suarez and Šimůnek* [1997] developed the following function for the reduction of the precipitation-dissolution rates due to surface poisoning by dissolved organic carbon, based on experimental data from *Inskip and Bloom* [1986]

$$r = \exp(-b_1x - b_2x^2 - b_3x^{0.5}) \quad (3.36)$$

where r is the reduction constant [-], x is dissolved organic carbon (μmol l⁻¹) and b_1 , b_2 , and b_3 are regression coefficients (0.005104, 0.000426, 0.069111, respectively).

3.8. Kinetic Model of Dolomite Dissolution

The reaction rates of dolomite dissolution, R^D (mmol cm⁻²s⁻¹), were calculated with the rate equation of *Busenberg and Plummer* [1982]

$$R^D = k_1 (H^+)^{0.5} + k_2 (H_2CO_3^*)^{0.5} + k_3 (H_2O)^{0.5} - k_4 (HCO_3^-) \quad (3.37)$$

where the temperature dependent first-order rate constants k_1 , k_2 , k_3 (mmol cm⁻²s⁻¹), representing the forward reactions, and k_4 (mmol cm⁻²s⁻¹), representing the back reaction, are given by (3.34) with empirical constants a_1 and a_2 given by *Busenberg and Plummer* [1982]. The dissolution rate R^D is again expressed in mmol of dolomite per cm² of surface area per second. These rate constants are used for ion activity products $IAP^D < 10^{-19}$. For values below 10^{-19} the rate is extremely small and assumed to be zero [*Busenberg and Plummer*, 1982] in the absence of additional data.

3.9. Silica Concentration in Soil Solution

Relatively little information exists about Si concentrations in soil water. Use of equilibrium calculations of silica solubility from the stable mineral (quartz) results in the unrealistic prediction that solution concentrations are independent of pH up to pH 8, above which the solubility will increase due to the dissociation of silicic acid. Si concentrations in soils are usually not fixed by quartz solubility but rather by dissolution (and possibly precipitation) of aluminosilicates including poorly crystallized phases and Si adsorption-desorption onto oxides and aluminosilicates. As a result of these reactions Si concentrations in soil solutions follow a U shaped curve with pH , similar to Al oxide solubility, with a Si minimum around pH 7.5 [Suarez, 1977]. Suarez [1977] developed a simple relation between silica content in the soil solution and the soil pH :

$$SiO_{4T} = d_1 + d_2 pH + d_3 pH^2 \quad (3.38)$$

in which the empirical constants d_1 , d_2 , and d_3 are equal to 6340, 1430, and 81.9, respectively, and where SiO_{4T} is the sum of all silica species expressed in $mol\ l^{-1}$. We utilize this expression and the dissociation expressions for K_{11} and K_{12} (eq. (3.13)) only to obtain estimates of H_4SiO_4 from total SiO_4 . As a result sepiolite reactions are not expressed in terms of $H_3SiO_4^-$ and $H_2SiO_4^{2-}$, which are not included in the charge balance expressions. Only the species H_4SiO_4 is used in the carbonate chemistry module.

3.10. Activity Coefficients

3.10.1. Extended Debye-Hückel Expression

Activity coefficient in the dilute to moderately saline solution range are calculated using the extended version of the Debye-Hückel equation [Truesdell and Jones, 1974]:

$$\ln \gamma = - \frac{Az^2 \sqrt{I}}{1 + Ba\sqrt{I}} + bI \quad (3.39)$$

where A ($kg^{0.5} mol^{-0.5}$) and B ($kg^{0.5} cm^{-1} mol^{-0.5}$) are constants depending only upon the dielectric constant, density, and temperature, z is the ionic charge in protonic units, a (cm) and b ($kg\ mol^{-1}$) are two adjustable parameters, and I is the ionic strength ($mol\ kg^{-1}$):

$$I = 0.5 \sum_{i=1}^M z_i^2 c_i \quad (3.40)$$

where M is the number of species in the solution mixture. The adjustable parameters a and b for individual species are given by *Truesdell and Jones* [1974]. The activities of neutral species are calculated as

$$\ln \gamma = a' I \quad (3.41)$$

where a' is an empirical parameter.

If the extended Debye-Hückel theory is used to calculate activity coefficients, the activity of water is then calculated in the same way as in the WATEQ program [*Truesdell and Jones, 1974*] using the approximate relation

$$a(\text{H}_2\text{O}) = 1 - 0.017 \sum_{i=1}^M m_i \quad (3.42)$$

3.10.2. Pitzer Expressions

At high ionic strength activity coefficients are no longer universal functions of ionic strength, but depend on the relative concentration of the various ions present in solution [*Felmy and Weare, 1986*]. The activity coefficients can then be expressed in terms of a virial-type expansion of the form [*Pitzer, 1979*]

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j B_{ij}(I)m_j + \sum_j \sum_k C_{ijk}m_j m_k + \dots \quad (3.43)$$

where γ_i^{DH} is a modified Debye-Hückel activity coefficient which is a universal function of ionic strength, and B_{ij} and C_{ijk} are specific coefficients for each interaction. The subroutines for calculation of the Pitzer activity coefficients were adopted from the GMIN code [*Felmy, 1990*]. This model is considered accurate also for solutions with very high ionic strength (up to 20 mol kg⁻¹), and can be used down to infinite dilution.

If the Pitzer theory is used, then the activity of water is obtained from the expression [*Felmy and Weare, 1986*]

$$\ln a(\text{H}_2\text{O}) = -\frac{W}{1000} \left(\sum_{i=1}^M m_i \right) \phi \quad (3.44)$$

where W is the molecular weight of water and ϕ the osmotic coefficient (defined in Section 3.12). We refer to *Felmy and Weare* [1986] for a more detailed discussion.

3.11. Temperature Effects

Most thermodynamic equilibrium constants depend on both the temperature and pressure of the system. The temperature dependence of the thermodynamic equilibrium constants is often expressed as a power function of the absolute temperature:

$$\log K = a_1 + \frac{a_2}{T} + a_3 T + a_4 \log T + \frac{a_5}{T^2} \quad (3.45)$$

where T is absolute temperature [K], and a_1 through a_5 are empirical constants. The pressure dependence can be neglected for most soils. The empirical constants for the temperature dependent thermodynamic constants used in the calculations are listed in Šimůnek *et al.* [1996]. The temperature dependence of the equilibrium constants for which the constants of equation (3.45) do not exist is expressed with the enthalpy of reaction and the Van 't Hoff expression [Truesdell and Jones, 1974].

3.12. Osmotic Coefficient and Osmotic Pressure Head

We use the semiempirical equation of Pitzer [1973] and co-workers to calculate the osmotic coefficient ϕ . The osmotic pressure of electrolyte solutions, P_ϕ (Pa), is related to the osmotic coefficient ϕ and molality as follows [Stokes, 1979]

$$P_\phi = RT \frac{M_s}{V_s} \frac{\nu m \phi}{m^0} \quad (3.46)$$

where V_s is the partial molar volume of the solvent ($\text{cm}^3 \text{mol}^{-1}$), m^0 is unit molality (1 mol kg^{-1}), and M_s is molar weight (mol^{-1}). The osmotic pressure head, h_ϕ [L], is related to the osmotic pressure by

$$h_\phi = \frac{P_\phi}{\rho g} \quad (3.47)$$

where ρ is the density of water [ML^{-3}] and g is the gravitational constant [$\text{L}^2 \text{T}^{-1}$].

3.13. Effect of Solution Composition on Hydraulic Conductivity

The accumulation of monovalent cations, such as sodium and potassium, often leads to clay dispersion, swelling, flocculation and overall poor soil physico-mechanical properties. These processes have an adverse effect on the soil hydraulic properties including hydraulic conductivity, infiltration rates and soil water retention as a result of swelling and clay dispersion. These

negative effects are usually explained based on the diffuse double layer theory. A consequence of the more diffuse double layer in the presence of monovalent ions as compared to divalent ions is the greater repulsion force or swelling pressure between neighboring clay platelets. These negative effects become more pronounced with decreasing salt concentration and valence of the adsorbed ions [Shainberg and Levy, 1992]. In addition, Suarez *et al.* [1984] determined that elevated levels of pH also had an adverse effect on the saturated hydraulic conductivity.

The effect of solution chemistry on the hydraulic conductivity in the major ion chemistry module is calculated as follows

$$K(h, pH, SAR, C_0) = r(pH, SAR, C_0) K(h) \quad (3.48)$$

where SAR is the sodium adsorption ratio, C_0 is the total salt concentration of the ambient solution in $\text{mmol}_c\text{L}^{-1}$, and r is a scaling factor which represents the effect of the solution composition on the final hydraulic conductivity [-], and which is related to pH , SAR and salinity. The hydraulic conductivity without the scaling factor r can be assumed to be the optimal value under favorable chemical conditions in terms of optimal pH , SAR and salinity. Although soil specific, the effects of solution chemistry are too important to ignore. We include reduction functions calculated for some illitic soils of California based on the experimental work of McNeal [1968] and Suarez *et al.* [1984]. The overall scaling factor r in equation (3.48) for this purpose is divided into two parts

$$r(pH, SAR, C_0) = r_1(SAR, C_0) r_2(pH) \quad (3.49)$$

where the first part, r_1 [-], reflects the effect of the exchangeable sodium percentage and dilution of the solution on the hydraulic conductivity, while the second part, r_2 [-], represents the effect of the soil solution pH . The first term is based on a simple clay-swelling model, which treats mixed-ions clays as simple mixture of homoionic sodium and calcium clay. Clay swelling is then related to a decrease in soil hydraulic conductivity [McNeal, 1974]. The r_1 term was defined by McNeal [1968] as

$$r_1 = 1 - \frac{cx^n}{1 + cx^n} \quad (3.50)$$

where c and n are empirical parameters, and x is a swelling factor. The interlayer swelling of soil montmorillonite, x , is defined in the following way

$$x = f_{mont} 3.6 \cdot 10^{-4} ESP^* d^* \quad (3.51)$$

where f_{mont} is the weight fraction of montmorillonite in the soil, d^* is the adjusted interlayer spacing [L] and ESP^* is the adjusted exchangeable sodium percentage. For most soils one can

use the assumption that $f_{mont} = 0.1$ [McNeal, 1968]. The adjusted exchangeable sodium percentage is calculated as

$$ESP^* = \max[0, ESP - (1.24 + 11.63 \log C_0)] \quad (3.52)$$

where C_0 is total salt concentration of the ambient solution in $\text{mmol}_c\text{l}^{-1}$, and ESP is defined as

$$ESP = 100 \frac{\overline{\text{Na}}}{CEC} \quad (3.53)$$

where CEC is the soil cation exchange capacity ($\text{mmol}_c\text{kg}^{-1}$) and $\overline{\text{Na}}$ the exchangeable sodium concentration ($\text{mmol}_c\text{kg}^{-1}$). The adjusted interlayer spacing, d^* , is given by

$$\begin{aligned} d^* &= 0 && \text{for } C_0 > 300 \text{ mmol}_c \text{ liter}^{-1} \\ d^* &= 356.4 C_0^{-1/2} + 1.2 && \text{for } C_0 < 300 \text{ mmol}_c \text{ liter}^{-1} \end{aligned} \quad (3.54)$$

McNeal [1968] reported that the values of the empirical factor n in equation (3.50) depends primarily on the soil ESP and that as a first approximation n values may be estimated using

$$\begin{aligned} n &= 1 && \text{for } ESP < 25 \\ n &= 2 && \text{for } 25 \leq ESP \leq 50 \\ n &= 3 && \text{for } ESP > 50 \end{aligned} \quad (3.55)$$

Only the values of the empirical factor c vary from soil to soil. HYDRUS uses values reported by McNeal [1968]:

$$\begin{aligned} c &= 35 && \text{for } ESP < 25 \\ c &= 932 && \text{for } 25 \leq ESP \leq 50 \\ c &= 25\,000 && \text{for } ESP > 50 \end{aligned} \quad (3.56)$$

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 using the r_1 values. The following equation was used

$$\begin{aligned} r_2 &= 1 && \text{for } pH < 6.83 \\ r_2 &= 3.46 - 0.36 pH && \text{for } 6.83 \leq pH \leq 9.3 \\ r_2 &= 0.1 && \text{for } pH > 9.3 \end{aligned} \quad (3.57)$$

Note, that although the models for reductions in the hydraulic conductivity due to changes in the solution composition were derived from data on the saturated hydraulic conductivity, the same reduction factors were used for the entire range of the pressure heads. The assumption that the r values for saturated conditions can be applied to the entire range of pressure heads has not been closely examined thus far in the literature.

4. Preprocessing

4.1. Solute Transport - General Information

When the UNSATCHEM module is used, basic information needed for defining the solute transport problem are entered in the **Solute Transport** dialog window displayed in Figure 4.1. In this window users specify again the **Space** and **Time Weighting Schemes**, and additional **Solute Information** such as mass units. Note that all concentrations in the UNSATCHEM module are either in meq/L (in the liquid phase) or meq/kg (in the solid phase) (meq=mmol_c). The pulse duration is not used in UNSATCHEM and the number of solutes is fixed to 8 (i.e., the number of considered major ions: Ca²⁺, Mg²⁺, Na⁺, K⁺, Alkalinity, SO₄²⁻, Cl⁻, and an independent tracer). The number of solution, adsorbed, and precipitated concentration combinations is specified when simulating the transport of major ions in the UNSATCHEM module. This value represents the maximum number of (solution, adsorbed, and precipitated) concentration combinations, which can be used to specify the initial and boundary (e.g., solution composition of rain water, water used for irrigation, groundwater, etc) conditions.

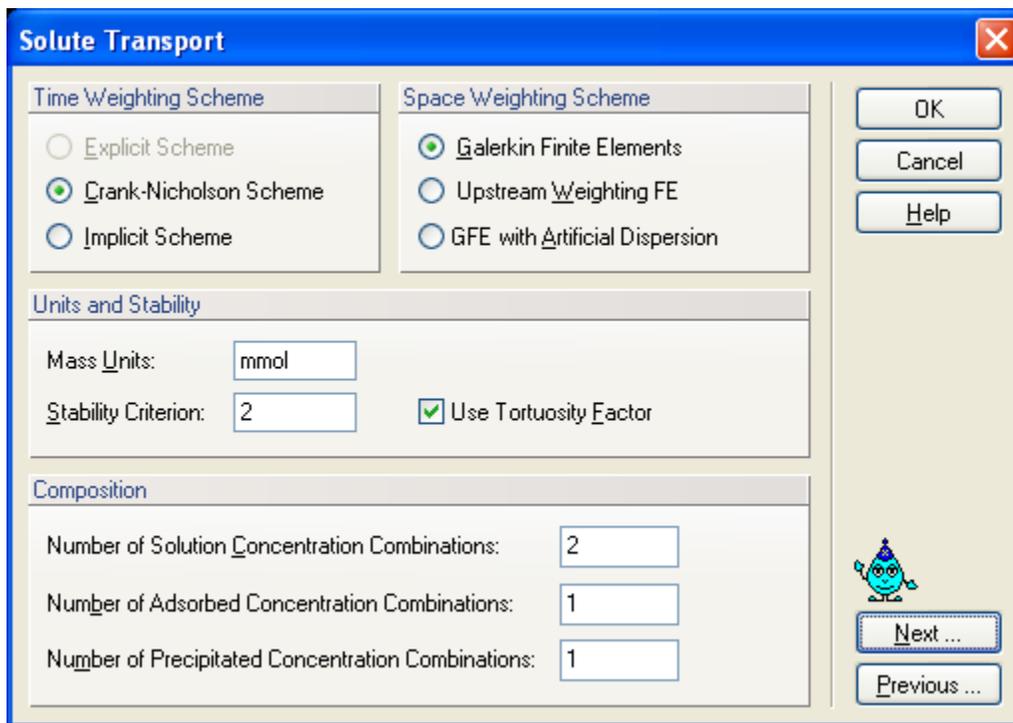


Figure 4.1. The Solute Transport dialog window for the UNSATCHEM module.

4.2. Solution Compositions for the UNSATCHEM Module

The set of **solution**, **adsorbed**, and **precipitated concentration combinations** for the UNSATCHEM module is specified in the **Solution Compositions** dialog window (Fig. 4.2). These (solution, adsorbed, and precipitated) concentration combinations can be used to specify

the initial and boundary conditions. The number of solution, adsorbed, and precipitated concentration combinations is specified in the **General Solute Transport Information** window (Fig. 4.1). **Solution Concentrations** need to be specified for all major ions: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Alkalinity, SO_4^{2-} , Cl^- , and an independent tracer; **Adsorbed Concentrations** for all cations: Ca^{2+} , Mg^{2+} , Na^+ , and K^+ ; and **Precipitated Concentrations** for all solids that UNSATCHEM can consider: calcite, dolomite, gypsum, nesquohonite, hydromagnesite, and sepiolite. **Solution Concentrations** need to be specified in meq/L (L = liter), and **Adsorbed Concentrations** and **Precipitated Concentrations** in meq/kg (meq=mmol_e).

Sol	Ca	Mg	Na	K	Alk	SO4	Cl	Tracer
1	2.63	1.05	2.55	0.06	2.33	2.03	1.94	1
2	12.2	9.66	37.5	0.27	6.5	22.1	31.1	0

Ads	Ca	Mg	Na	K
1	50	20	9	1

Prec	Calcite	Gypsum	Dolomite	HydroMg	Nesqoh	Sepiolite
1	500	200	0	0	0	0

Figure 4.2. The Solution Compositions dialog window for the UNSATCHEM module.

4.3. Solute Reaction Parameters

When the UNSATCHEM module is used, the *Solute Reaction* (and *transport*) *Parameters* are specified in the **Solute Reaction Parameters** dialog window displayed in Figure 4.3. The following **Soil Specific Parameters** are specified for each soil material:

- Bulk.d.** Bulk density, ρ [g/cm^3]
- Dw** Molecular diffusion coefficient in free water, D_w [L^2T^{-1}]
- Disper.L.** Longitudinal dispersivity, D_L [L]
- Disper.T.** Transverse dispersivity, D_T [L]
- CEC** Cation exchange capacity, CEC [meq/kg]

Calc.SA	Calcite surface area [m^2/dm^3]
Dol.SA	Dolomite surface area [m^2/dm^3]
DOC	Dissolved organic carbon [$\mu\text{mol}/\text{dm}^3$]
K[Ca/Mg]	Gapon constant for exchange of calcium and magnesium
K[Ca/Na]	Gapon constant for exchange of calcium and sodium
K[Ca/K]	Gapon constant for exchange of calcium and potassium

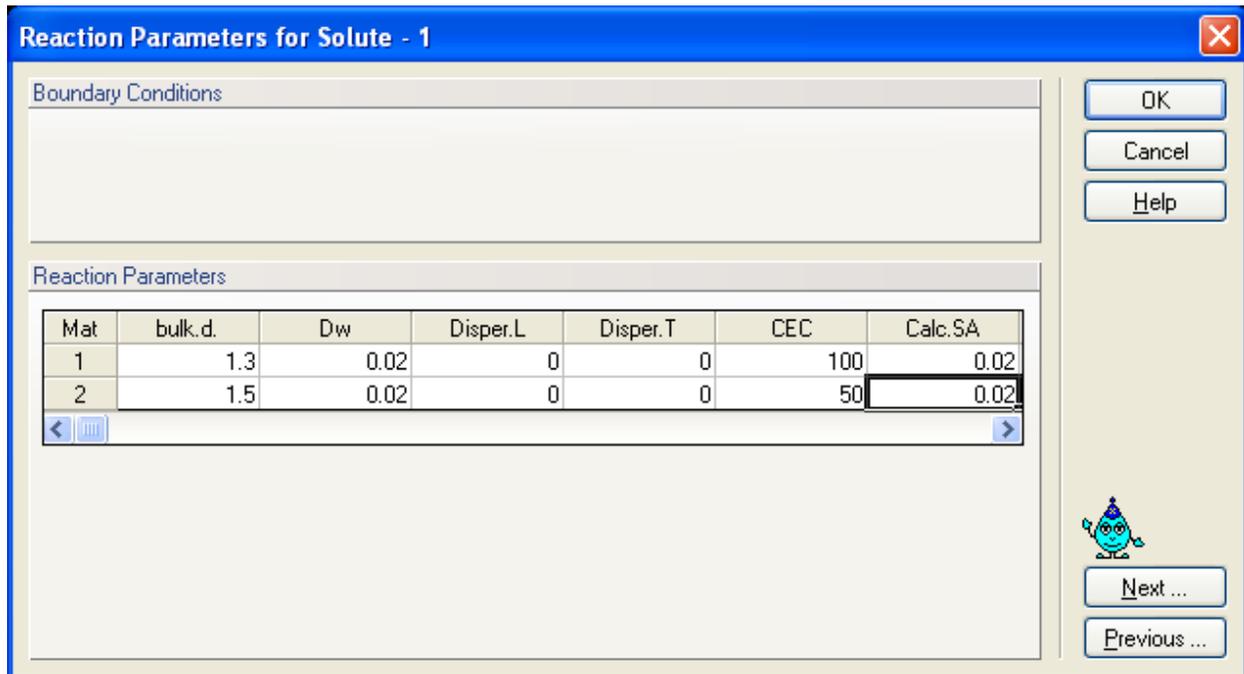


Figure 4.3. The Solute Reaction Parameters dialog window for the UNSATCHEM module.

4.4. Chemical Parameters for the UNSATCHEM module.

The following chemical parameters and selections for the UNSATCHEM module are specified in the **Chemical Parameters** dialog window (Fig. 4.4):

- Whether the kinetic or equilibrium model for the precipitation and dissolution of calcite and dissolution of dolomite is to be used (the **Kinetic Precipitation/Dissolution** check box).
- Whether the silica content in the solution is to be calculated based on the solution pH, or whether the effect of pH is to be neglected (the **Silica in Solution (pH Dependency)** check box).
- The **Critical Ionic Strength**, i.e., the ionic strength, below which the extended Debye-Hückel equation is used to calculate ion activity coefficients. Pitzer virial-type equations are used above this value.
- The **Maximum Number of Iterations** allowed during any time step between the solute transport and chemical modules. When the maximum number of iterations is reached then the code proceeds to the new time level. The recommended value (if the iterative approach

is to be used; from our experience) is 5. Set equal to one if no iteration (we recommend this non-iterative approach) is required (this, in general, leads to significantly lower computational time without significantly altering the results in most cases).

- Whether the hydraulic conductivity is to be modified depending on the solution chemistry using the *McNeal* [1968] semi-empirical approach (the **Conductivity Reduction due to Chemistry** check box).

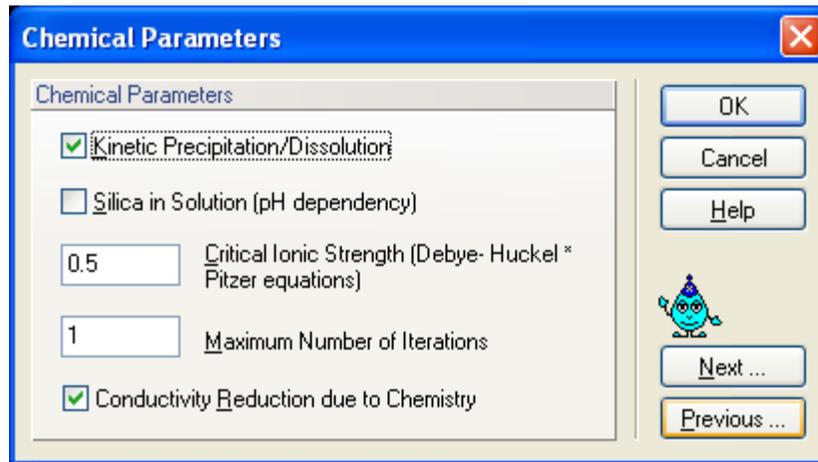


Figure 4.4. The Chemical Parameters dialog window for the UNSATCHEM module.

4.5. Initial Conditions

The initial conditions for the UNSATCHEM module are defined in terms of the Solution Composition numbers (integer), Exchange Species numbers, Solid Species numbers and CO2 Concentrations (real). The composition numbers refer to different Solution Compositions, Exchange Species and Solid Species defined in Figure 4.2.

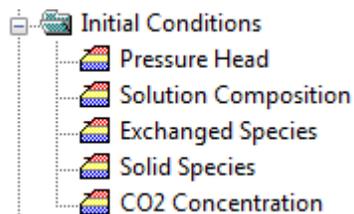


Figure 4.5. The "Initial Conditions" part of Data Tab of the Navigator Bar for the UNSATCHEM module.

5. Post-processing

5.1. Results – Graphical Display

Multiple variables can be displayed in the View window (Fig. 5.1). A comprehensive list of variables that can be displayed in the View window is summarized in Tables 5.1, respectively.

Table 5.1. Additional UNSATCHEM variables displayed in the View Window of the Results tab (Results - Graphical Display).

Variable	Description
UNSATCHEM Variables	Major ions (Ca, Mg, Na, K, HCO ₃ , SO ₄ , Cl [in mmol _c l ⁻¹], tracer [-], sorbed Ca, sorbed Mg, sorbed Na, sorbed K, calcite, gypsum, dolomite, nesquohonite, hydromagnesite, sepiolite (in mmol _c kg ⁻¹), pH [-], EC [dS/m], and SAR.



Figure 5.1. The "Results - Graphical Display" part of Data Tab of the Navigator Bar for the UNSATCHEM module.

5.2. Results – Other Information

The *Chemical Mass Balance information* (Fig. 5.2) (on the **Data Tab** of the **Navigator Bar** or at the **Results Menu**) is provided for the UNSATCHEM module. This file gives mass balances in different phases (liquid, sorbed, solid) for all major ions (i.e., Ca, Mg, Na, K, HCO₃, SO₄, and Cl).

Time [T]: 0.0000

	Ca	Mg	Na	K	HCO3	SO4	Cl	Tracer
Boundary fluxes [VM/L3]	0.000E+00							
Mass in solution [VM/L3]	0.190E+07	0.000E+00	0.849E+07	0.000E+00	0.111E+06	0.889E+07	0.139E+07	0.000E+00
Mass adsorbed [VM/L3]	0.781E+07	0.555E-11	0.525E+07	0.277E-11	-	-	-	-
Mass in solid [VM/L3]	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	-	-
Total mass [VM/L3]	0.971E+07	0.555E-11	0.137E+08	0.277E-11	0.111E+06	0.889E+07	0.139E+07	0.000E+00

Time [T]: 0.0500

	Ca	Mg	Na	K	HCO3	SO4	Cl	Tracer
Boundary fluxes [VM/L3]	0.700E+03	0.000E+00	0.176E+05	0.000E+00	0.148E+04	-0.183E+03	0.170E+05	0.370E+02
Mass in solution [VM/L3]	0.190E+07	0.000E+00	0.851E+07	0.000E+00	0.112E+06	0.889E+07	0.141E+07	0.368E+02
Mass adsorbed [VM/L3]	0.781E+07	0.555E-11	0.524E+07	0.278E-11	-	-	-	-
Mass in solid [VM/L3]	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	-	-
Total mass [VM/L3]	0.971E+07	0.555E-11	0.138E+08	0.278E-11	0.112E+06	0.889E+07	0.141E+07	0.368E+02
Absolute error [VM/L3]	-0.147E+04	-0.330E-14	0.900E+03	-0.165E-14	0.111E+03	-0.478E+03	-0.650E+01	0.136E+00
Relative error [%]	0.015	0.059	0.007	0.059	0.099	0.005	0.000	0.368

Time [T]: 0.1000

	Ca	Mg	Na	K	HCO3	SO4	Cl	Tracer
Boundary fluxes [VM/L3]	0.104E+04	0.000E+00	0.265E+05	0.000E+00	0.223E+04	-0.366E+03	0.257E+05	0.560E+02
Mass in solution [VM/L3]	0.189E+07	0.000E+00	0.852E+07	0.000E+00	0.113E+06	0.889E+07	0.141E+07	0.558E+02

OK

Figure 5.2. The Chemical Mass Balance Information dialog window for the UNSATCHEM module.

6. Input and Output Files

The UNSATCHEM module requires several additional input files (described in Section 6.1 below) providing various coefficients for calculating ion activities using the Pitzer's expressions and has a slightly different format of the Selector.in file (described in Section 6.2 below) in the section related to solute transport.

6.1. Pitzer's Coefficients

The major ion chemistry module requires four additional input files containing input data for the Pitzer equations. These four input files are provided together with the program and should not be changed by the user. The four input files, which were adopted from *Felmy* [1990], are placed in the ChemData directory under the executable program.

COMP.DAT	contains the species ID numbers, species names, and species charge.
BINARYP.DAT	contains the ID number of each species in each binary interaction considered (e.g., CaHCO_3^+) and the Pitzer ion interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ for binary systems.
TERNARYP.DAT	contains the Pitzer ion-interaction parameters for the common ion ternary systems, θ , and ψ . The first two columns include the cation-cation or anion-anion ID numbers associated with the ion-interaction parameter, θ , in column three. Subsequent columns include the anion or cation ID number and the triple ion-interaction parameter, ψ , associated with that triple ion interaction.
LAMBDA.DAT	contains the Pitzer ion-interaction parameters for the neutral species, λ and δ . The first column of this file contains the ID number for the neutral species, and the second column the ID number for the cation or anion involved in the neutral-cation or neutral-anion interaction parameterized by the Pitzer λ parameter included in the third column. Subsequent columns are for higher-order neutral interactions.

6.2. The Selector.in Input File

HYDRUS (2D/3D) with UNSATCHEM module has a different structure of the part of the Selector.in file that is related to solute transport. This is described in detail in Table 6.1.

Table. 6.1. Major ion chemistry information in the Selector.in input file.

Record	Type	Variable	Description
1,2	-	-	Comment lines.
3	Real	<i>Epsi</i>	Temporal weighing coefficient. =0.0 for an explicit scheme, =0.5 for a Crank-Nicholson implicit scheme. =1.0 for a fully implicit scheme.
3	Logical	<i>IUpW</i>	.true. if upstream weighing formulation is to be used (see Section 6.4.2 of the HYDRUS technical manual). .false. if the original Galerkin formulation is to be used.
3	Logical	<i>lArtD</i>	.true. if artificial dispersion is to be added in order to fulfill the <i>PeCr</i> stability criterion (see Section 6.4.6 of the HYDRUS technical manual). .false. otherwise.
3	Real	<i>PeCr</i>	Stability criteria (see Section 6.4.6 of the HYDRUS technical manual). Set equal to zero when <i>IUpW</i> is equal to .true. .
4	-	-	Comment line.
5	Logical	<i>lRate</i>	Set this logical variable equal to .true. if kinetic precipitation-dissolution of calcite and kinetic dissolution of dolomite is to be considered. Set this logical variable equal to .false. if only equilibrium reactions are to be considered.
5	Logical	<i>lSilic</i>	Set this logical variable equal to .true. if the silica content of the soil solution is to be calculated based on the solution <i>pH</i> . Set this logical variable equal to .false. if the silica content of the soil solution is not considered.
5	Real	<i>UCrit</i>	Value of ionic strength below which the extended Debye-Hückel equation is used to calculate ion activity coefficients. Pitzer's virial-type equations are used above this value. It is suggested that either one or the other be used.
5	Integer	<i>MaxCh</i>	Maximum number of iterations allowed during any time step between the solute transport and chemical modules. When the maximum number of iterations is reached for <i>MaxCh</i> >5 then the time step is divided by three and the particular time level is restarted again. When the maximum number of iterations is reached for <i>MaxCh</i> ≤5 then the code proceeds to the new time level. Recommended value (from experience) is 5. Set equal to one if no iteration is required.
5	Logical	<i>lkRed</i>	Set this logical variable equal to .true. if hydraulic conductivity is to be adjusted depending on the solution chemistry (see Section 3.13). Set this logical variable equal to .false. if hydraulic conductivity is not to be adjusted depending on the solution chemistry (see Section 3.13)..
6	-	-	Comment line.
7	Real	<i>ChPar(1,M)</i>	Bulk density of material <i>M</i> [g/cm ³].
7	Real	<i>ChPar(2,M)</i>	Molecular diffusion coefficient in free water, <i>D_w</i> [L ² T ⁻¹].
7	Real	<i>ChPar(3,M)</i>	Longitudinal dispersivity for material type <i>M</i> , <i>D_L</i> [L].
7	Real	<i>ChPar(4,M)</i>	Transverse dispersivity for material type <i>M</i> , <i>D_T</i> [L].
7	Real	<i>ChPar(5,M)</i>	Cation exchange capacity for material type <i>M</i> , <i>c_T</i> (mmol _c kg ⁻¹ of soil).
7	Real	<i>ChPar(6,M)</i>	Calcite surface area <i>A^C</i> (m ² l ⁻¹ of soil matrix). Set this variable equal to zero when <i>lRate</i> = .false. .

Table 6.1. (continued)

Record	Type	Variable	Description
7	Real	<i>ChPar(7,M)</i>	Dolomite surface area A^D (m^2l^{-1} of soil matrix). Set this variable equal to zero when <i>lRate</i> = false . or dolomite is not present in the soil profile.
7	Real	<i>ChPar(8,M)</i>	Dissolved organic carbon ($\mu\text{mol l}^{-1}$). This variable is used to calculate the reduction in the precipitation-dissolution rates of calcite.
7	Real	<i>ChPar(9,M)</i>	Gapon' selectivity constant between calcium and magnesium, K_{13} [-].
7	Real	<i>ChPar(10,M)</i>	Gapon' selectivity constant between calcium and sodium, K_{14} [-].
7	Real	<i>ChPar(11,M)</i>	Gapon' selectivity constant between calcium and potassium, K_{15} [-].
			Record 7 information is provided for each material <i>M</i> (from 1 to <i>NMat</i>).
8	-	-	Comment line.
9	Integer	<i>nSolConc</i>	Number of different solutions used in a particular application.
9	Integer	<i>nAdsConc</i>	Number of surface species combinations used in a particular application.
9	Integer	<i>nPrecConc</i>	Number of mineral phase combinations used in a particular application.
10	-	-	Comment line.
11	Real	<i>ConcTab(1,1)</i>	Analytical concentration of calcium for the first solution concentration combination, Ca_T ($\text{mmol}_c\text{l}^{-1}$ of solution).
11	Real	<i>ConcTab(1,2)</i>	Analytical concentration of magnesium for the first solution concentration combination, Mg_T ($\text{mmol}_c\text{l}^{-1}$ of solution).
11	Real	<i>ConcTab(1,3)</i>	Analytical concentration of sodium for the first solution concentration combination, Na_T ($\text{mmol}_c\text{l}^{-1}$ of solution).
11	Real	<i>ConcTab(1,4)</i>	Analytical concentration of potassium for the first solution concentration combination, K_T ($\text{mmol}_c\text{l}^{-1}$ of solution).
11	Real	<i>ConcTab(1,5)</i>	Analytical concentration of alkalinity for the first solution concentration combination, <i>Alk</i> ($\text{mmol}_c\text{l}^{-1}$ of solution).
11	Real	<i>ConcTab(1,6)</i>	Analytical concentration of sulfate for the first solution concentration combination, SO_{4T} ($\text{mmol}_c\text{l}^{-1}$ of solution).
11	Real	<i>ConcTab(1,7)</i>	Analytical concentration of chloride for the first solution concentration combination, Cl_T ($\text{mmol}_c\text{l}^{-1}$ of solution).
11	Real	<i>ConcTab(1,8)</i>	Analytical concentration of hypothetical tracer for the first solution concentration combination [-].
			In general, one record as described above is required for each solution concentration combination, starting with the first solution concentration combination and continuing in sequence up to the <i>nSolConc</i> combination.
12	-	-	Comment line.
13	Real	<i>XConcTab(1,1)</i>	Adsorbed (surface species) calcium concentration for the first surface species combination, <i>a</i> ($\text{mmol}_c\text{kg}^{-1}$ of soil matrix).
13	Real	<i>XConcTab(1,2)</i>	Adsorbed magnesium concentration for the first surface species combination, <i>g</i> ($\text{mmol}_c\text{kg}^{-1}$ of soil matrix).
13	Real	<i>XConcTab(1,3)</i>	Adsorbed sodium concentration for the first surface species combination, <i>a</i> ($\text{mmol}_c\text{kg}^{-1}$ of soil matrix).
13	Real	<i>XConcTab(1,4)</i>	Adsorbed potassium concentration for the surface species combination, ($\text{mmol}_c\text{kg}^{-1}$ of soil matrix).

Table 6.1. (continued)

Record	Type	Variable	Description
			In general, one record as described above is required for each surface species combination, starting with the first surface species combination and continuing in sequence up to the <i>nAdsConcth</i> combination.
14	-	-	Comment line.
15	Real	<i>SConcTab</i> (1,1)	Solid phase calcite concentration for the first mineral phase combination expressed in mmol _c of Ca per kg of soil matrix, CaCO ₃ (divide by 2*10 ⁻³ to obtain moles of calcite per kg of soil matrix).
17	Real	<i>SConcTab</i> (1,2)	Solid phase gypsum concentration for the first mineral phase combination expressed in mmol _c of Ca per kg of soil matrix, CaSO ₄ (divide by 2*10 ⁻³ to obtain moles of gypsum per kg of soil matrix).
17	Real	<i>SConcTab</i> (1,3)	Solid phase dolomite concentration for the first mineral phase combination expressed in mmol _c of Ca per kg of soil matrix, CaMg(CO ₃) ₂ (divide by 2*10 ⁻³ to obtain moles of dolomite per kg of soil matrix).
17	Real	<i>SConcTab</i> (1,4)	Solid phase hydromagnesite concentration for the first mineral phase combination expressed in mmol _c of Mg per kg of soil matrix, Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O (divide by 10 ⁻⁴ to obtain moles of hydromagnesite per kg of soil matrix).
17	Real	<i>SConcTab</i> (1,5)	Solid phase nesquehonite concentration for the first mineral phase combination expressed in mmol _c of Mg per kg of soil matrix, MgCO ₃ ·3H ₂ O (divide by 2*10 ⁻³ to obtain moles of nesquehonite per kg of soil matrix).
17	Real	<i>SConcTab</i> (1,6)	Solid phase sepiolite concentration for the first mineral phase combination expressed in mmol _c of Mg per kg of soil matrix, Mg ₂ Si ₃ O _{7.5} (OH)·3H ₂ O (divide by 4*10 ⁻³ to obtain moles of nesquehonite per kg of soil matrix).
			In general, one record as described above is required for each mineral phase combination, starting with the first mineral phase combination and continuing in sequence up to the <i>nPrecConcth</i> combination.

6.3. UNSATCHEM Output Files

The UNSATCHEM module prints at prescribed print times, in addition to output printed by the standard HYDRUS module, the following files:

CONC <i>i</i> .OUT	Nodal values of the aqueous concentrations of calcium, magnesium, sodium, potassium, alkalinity, sulfate, chloride ($\text{mmol}_c\text{L}^{-1}$), and hypothetical tracer [-] (where $i=1$ through 8)
SORBi.OUT	Nodal values of the mineral phase concentrations for calcite, gypsum, dolomite, hydromagnesite, nesquehonite, and sepiolite, and nodal values of the adsorbed concentrations for calcium, magnesium, sodium, and potassium ($\text{mmol}_c\text{kg}^{-1}$) (where $i=1$ through 10). Adsorbed concentrations are printed only when cation exchange is considered.
EQUIL.OUT	This file contains the chemical information such as activities of calcium, bicarbonate and water, alkalinity, <i>pH</i> , <i>SAR</i> , electric conductivity of the solution, ionic strength, osmotic coefficient, osmotic pressure head, and ion activity products for calcite, gypsum and dolomite (see Table 6.2).
CHEMBAL.OUT	This file contains the information about the total amount of particular species (e.g. Ca, Mg, SO ₄ ,...) in solution, mineral phase and surface species form in the entire flow region, as well as the cumulative boundary fluxes and absolute mass error in particular species. All mass balances and cumulative solute fluxes are expressed in units of meq/m or meq for two- or three-dimensional applications, respectively.
PH.OUT	Nodal values of <i>pH</i> .
SAR.OUT	Nodal values of Sodium Adsorption Ratio (<i>SAR</i>).
EC.OUT	Nodal values of Electric Conductivity (<i>EC</i>) (dSm^{-1}).

Table 6.2. EQUIL.OUT - chemical information.

<i>Node</i>	Number of nodal point <i>n</i> .
<i>Width</i>	<i>x</i> -coordinate of node <i>n</i> [L].
<i>Depth</i>	<i>y</i> -coordinate of node <i>n</i> [L].
<i>aCa</i>	Activity of Ca ²⁺ [-].
<i>aHCO₃</i>	Activity of HCO ₃ ⁻ [-].
<i>aH₂O</i>	Activity of water [-].
<i>Alk</i>	Alkalinity (mmol _c kg ⁻¹).
<i>pH</i>	Negative logarithm of hydrogen activity, -log(H), [-].
<i>SAR</i>	Sodium adsorption ratio, defined as [Na/(Ca+Mg) ^{0.5}] (mmol ^{0.5} l ^{-0.5}).
<i>EC</i>	Electric conductivity of the soil solution (dSm ⁻¹) (calculated using the method 3 of McNeal <i>et al.</i> , 1970).
<i>U</i>	Ionic strength (mol kg ⁻¹).
<i>pIAP(c)</i>	Negative logarithm of the ion activity product for calcite, -log[(Ca ²⁺)(CO ₃ ²⁻)], [-].
<i>pIAP(g)</i>	Negative logarithm of the ion activity product for gypsum, -log[(Ca ²⁺)(SO ₄ ²⁻)(H ₂ O) ²], [-].
<i>pIAP(d)</i>	Negative logarithm of the ion activity product for dolomite, -log[(Ca ²⁺)(Mg ²⁺)(CO ₃ ²⁻) ²], [-].
<i>phi</i>	Osmotic coefficient [-].
<i>hphi</i>	Osmotic pressure head [m].

7. Example Problems

The module UNSATCHEM is developed from the variably saturated solute transport model, and thus the water flow and solute transport parts of the model have been tested earlier. Therefore both example problems solved in this section concentrate on the demonstration of the chemical features of the model.

Two example problems are presented in this section. The first example simulates an infiltration process into a relatively dry soil column. This example shows predicted differences between the equilibrium and kinetic precipitation-dissolution model. The second example simulates a furrow irrigation problem

7.1. Example 1 - Column Infiltration

This example is based on the one used in the documentation of the code SWMS_2D [Šimůnek *et al.*, 1992] to compare results obtained with the SWMS_2D and UNSAT2 [Davis and Neuman, 1983] codes. It originally simulated a one-dimensional laboratory infiltration experiment discussed by Skaggs *et al.* [1970]. This example was altered for the purposes of this report to include multicomponent chemical transport.

The soil water retention and relative hydraulic conductivity functions of the sandy soil are $\theta_r=0.02$, $\theta_a=-0.02$, $\theta_s=\theta_m=0.35$, $\theta_k=0.2875$, $\alpha=0.0410 \text{ cm}^{-1}$, $n=1.964$, $K_s=0.000722 \text{ cm s}^{-1}$, $K_k=0.000695 \text{ cm s}^{-1}$). The sand was assumed to be at an initial pressure head of -150 cm. The soil hydraulic properties were assumed to be homogenous and isotropic. The column was subjected to ponded infiltration (a Dirichlet boundary condition) at the soil surface, resulting in one-dimensional vertical water flow. The open bottom boundary of the soil column was simulated by implementing a no-flow boundary condition during unsaturated flow ($h<0$), and a seepage face with $h=0$ when the bottom boundary becomes saturated (this last condition was not reached during the simulation). The solution composition of the water initially present in the soil profile is that of a calcite supersaturated well water from the Wellton-Mohawk Irrigation District (well # 15 [Suarez, 1977]: $\text{Ca}_T=12.2$, $\text{Mg}_T=9.7$, $\text{Na}_T=37.5$, $\text{K}_T=0.3$, $\text{Cl}_T=31.1$, $\text{SO}_{4T}=22.1$, $\text{alkalinity}=6.5 \text{ mmol}_c\text{L}^{-1}$). Calcite undersaturated Colorado river water from the Grand Valley ([Rhoades and Suarez, 1977]: $\text{Ca}_T=2.63$, $\text{Mg}_T=1.05$, $\text{Na}_T=2.55$, $\text{K}_T=0.06$, $\text{Cl}_T=1.94$, $\text{SO}_{4T}=2.03$, $\text{alkalinity}=2.33 \text{ mmol}_c\text{L}^{-1}$) was used as the solution composition of the infiltrating water. The simulation was run at a temperature of 25 °C and the soil CO₂ concentration was assumed to be equal to the atmospheric CO₂ (0.000333). The precipitation-dissolution of calcite was considered either as an equilibrium or kinetic process with a calcite surface area of $0.02 \text{ m}^2\text{L}^{-1}$ of soil. The bulk density of the soil was taken as 1.3 g cm^{-3} and molecular diffusion as $0.02 \text{ cm}^2\text{s}^{-1}$. Longitudinal dispersivity was equal to zero. Activity coefficients were calculated with the Debye-Hückel equation. Cation exchange was not considered in this example.

Figures 7.1 and 7.2 show the water content and tracer concentration profiles, respectively, at various times. Calcium concentration and alkalinity profiles at various times for both equilibrium and kinetic calcite precipitation-dissolution are shown in Figures 7.3 and 7.4, respectively. Calcite profiles at various times for both equilibrium and kinetic calcite precipitation-dissolution are shown in Figure 7.5.

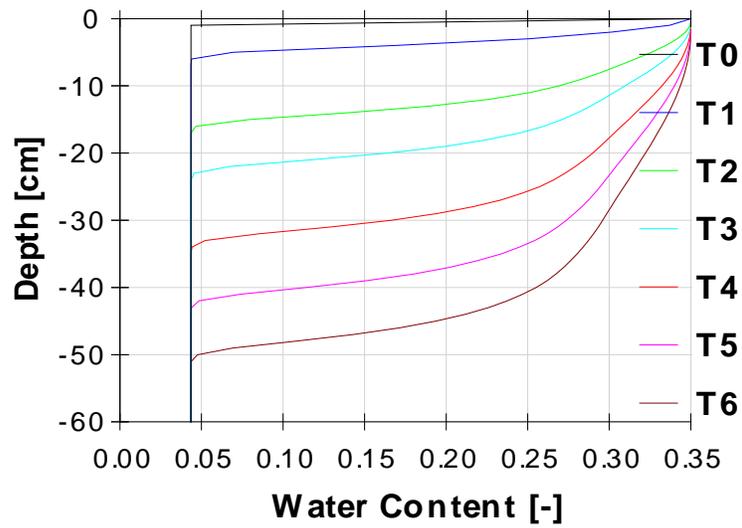


Figure 7.1. Water content profiles at various times for example 1.

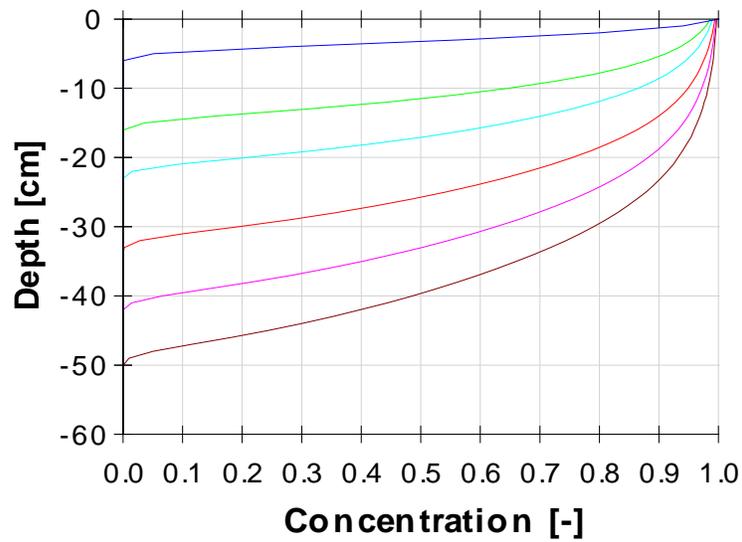


Figure 7.2. Tracer concentration profiles at various times for example 1.

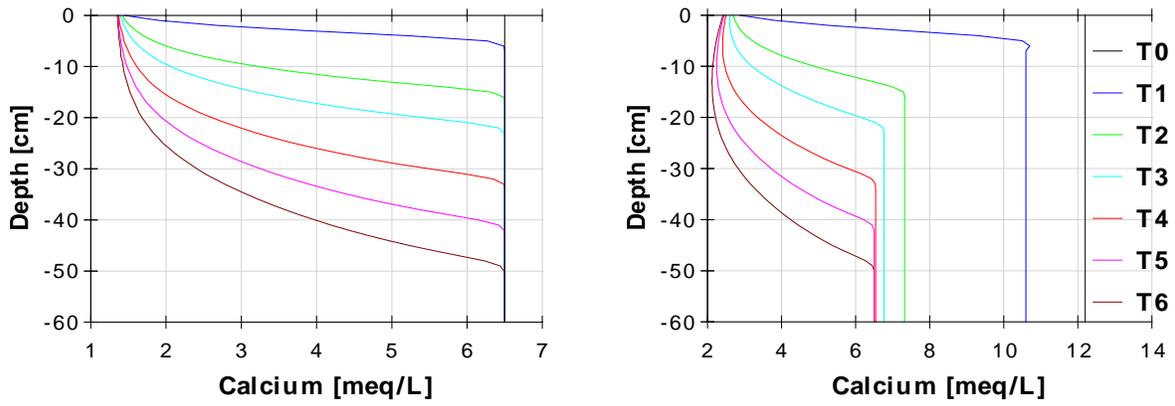


Figure 7.3. Calcium concentration profiles at various times for equilibrium (left) and kinetic (right) calcite precipitation-dissolution for example 1.

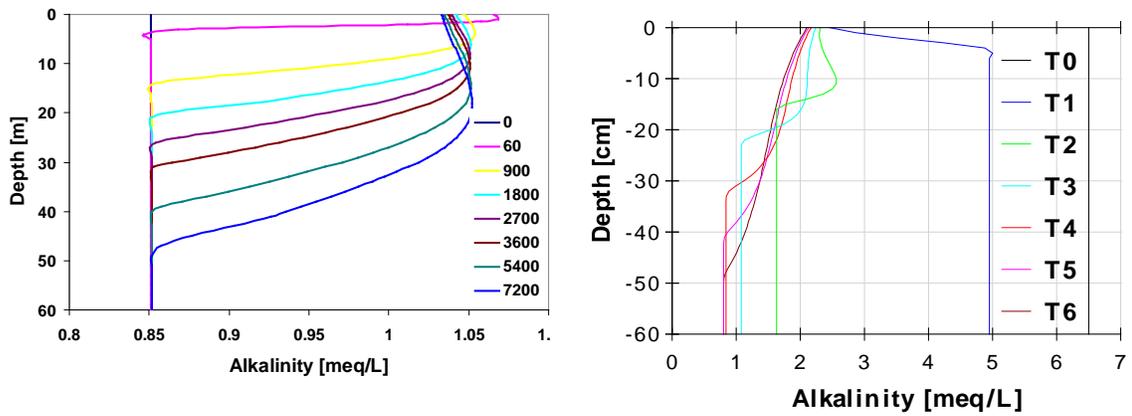


Figure 7.4. Alkalinity profiles at various times for equilibrium (left) and kinetic (right) calcite precipitation-dissolution for example 1.

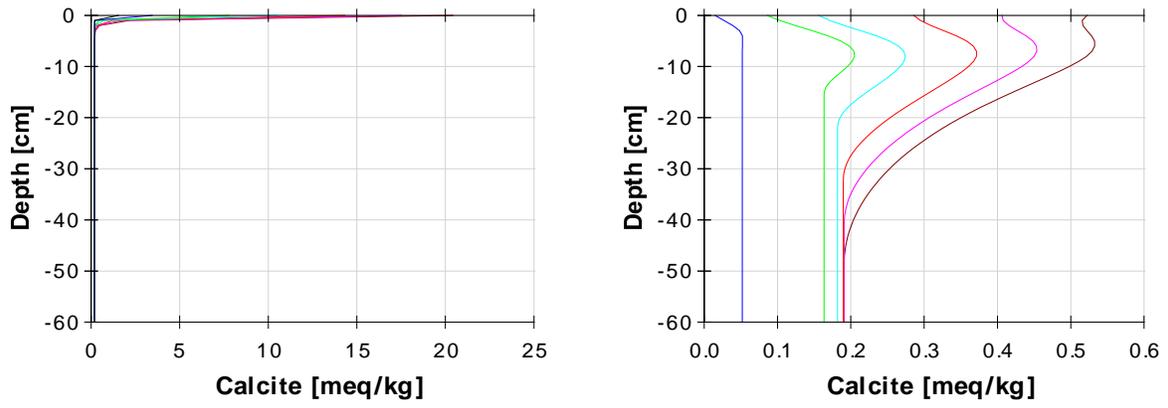


Figure 7.5. Calcite profiles at various times for equilibrium (left) and kinetic (right) calcite precipitation-dissolution for example 1.

7. 2. Example 2 - Two-Dimensional Furrow Irrigation Problem

A furrow irrigation problem was used to simulate two-dimensional infiltration of gypsum saturated water into a sodic soil. The simulation of sodic soil reclamation demonstrates the cation exchange feature of UNSATCHEM. The schematic representation of the flow domain for the considered furrow irrigation together with the finite element mesh is presented in Figure 7.6. It is assumed that every other furrow is flooded with water and that the water level in the irrigated furrow is kept constant at a level of 6 cm. Due to symmetry, it is necessary to carry out the simulation only for the domain between the axis of two neighboring furrows. Free drainage is used as the bottom boundary condition and zero flux is considered on the rest of the boundary. The initial pressure head condition is -200 cm and the soil hydraulic properties are the same as those used in the second example.

The calculation was run at a constant temperature of 25 °C and a CO₂ concentration of 0.01 cm³cm⁻³. Root water uptake and evaporation were neglected. The bulk density of the soil was taken as 1.4 g cm⁻³ and molecular diffusion as 2 cm²day⁻¹. Longitudinal and transverse dispersivities were equal to 2 and 0.2 cm, respectively.

The solution composition of the water initially present in the soil profile is that of the following highly sodic water: Ca_T=0.2, Mg_T=0.0, Na_T=4.8, K_T=0.0, Cl_T=4.6, SO_{4T}=0.0, Alk=0.4 mmol_cL⁻¹. The cation exchange capacity is equal to 100 mmol_ckg⁻¹ and is divided between exchangeable calcium and sodium (a=5.0, a=95.0 mmol_ckg⁻¹). The Gapon selectivity coefficients from *Wagenet and Hutson* [1987] were used ($K_{13}=0.896$, $K_{14}=1.158$, $K_{15}=0.111$). The solution composition of the irrigation water was almost gypsum saturated: Ca_T=32.6, Mg_T=0.0, Na_T=4.8, K_T=0.0, Cl_T=5.0, SO_{4T}=32.0, Alk=0.4 mmol_cL⁻¹. As a consequence of the reactions of the irrigation water with the exchanger composition, cation exchange was the dominant chemical processes in the soil profile. Cation exchange is treated as an instantaneous process in the model.

Figure 7.7 shows the pressure head profiles for four different times. The distribution of the hypothetical tracer is shown on Figure 7.8. Figures 7.9 and 7.10 present the exchangeable concentrations of calcium and sodium, respectively. The exchange phase concentrations reflect the changes in aqueous Na and Ca concentration. Note the significant lagging of the exchanger front to both the water and tracer front. Also due to the high nonlinearity of Na-Ca exchange, the concentration and exchange fronts are very sharp, in contrast to the more diffuse tracer fronts. After 5 days less than 25% of the profile has been reclaimed to exchangeable sodium percentage less than 15 (which has been the criteria defining the designation sodic soil). The selected cation exchange capacity of 100 mmol_ckg⁻¹ is relatively low. Selection of a higher exchange capacity and associated hydraulic properties of a finer textured soil would enhance both the time required for infiltration, as well as quantity of water required for reclamation.

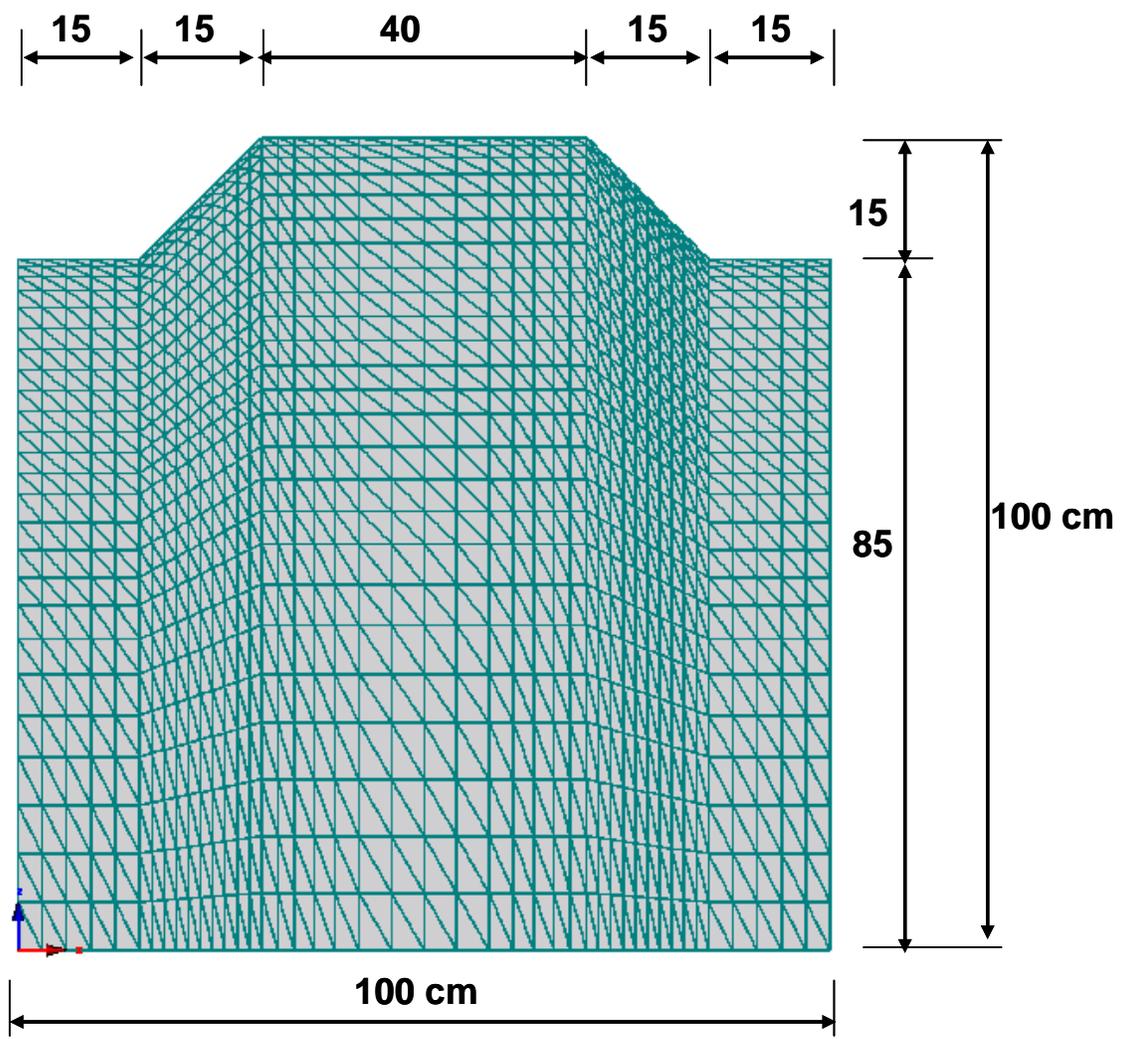


Figure 7.6. Schematic representation and finite element mesh of the flow domain for the furrow irrigation system for example 2.

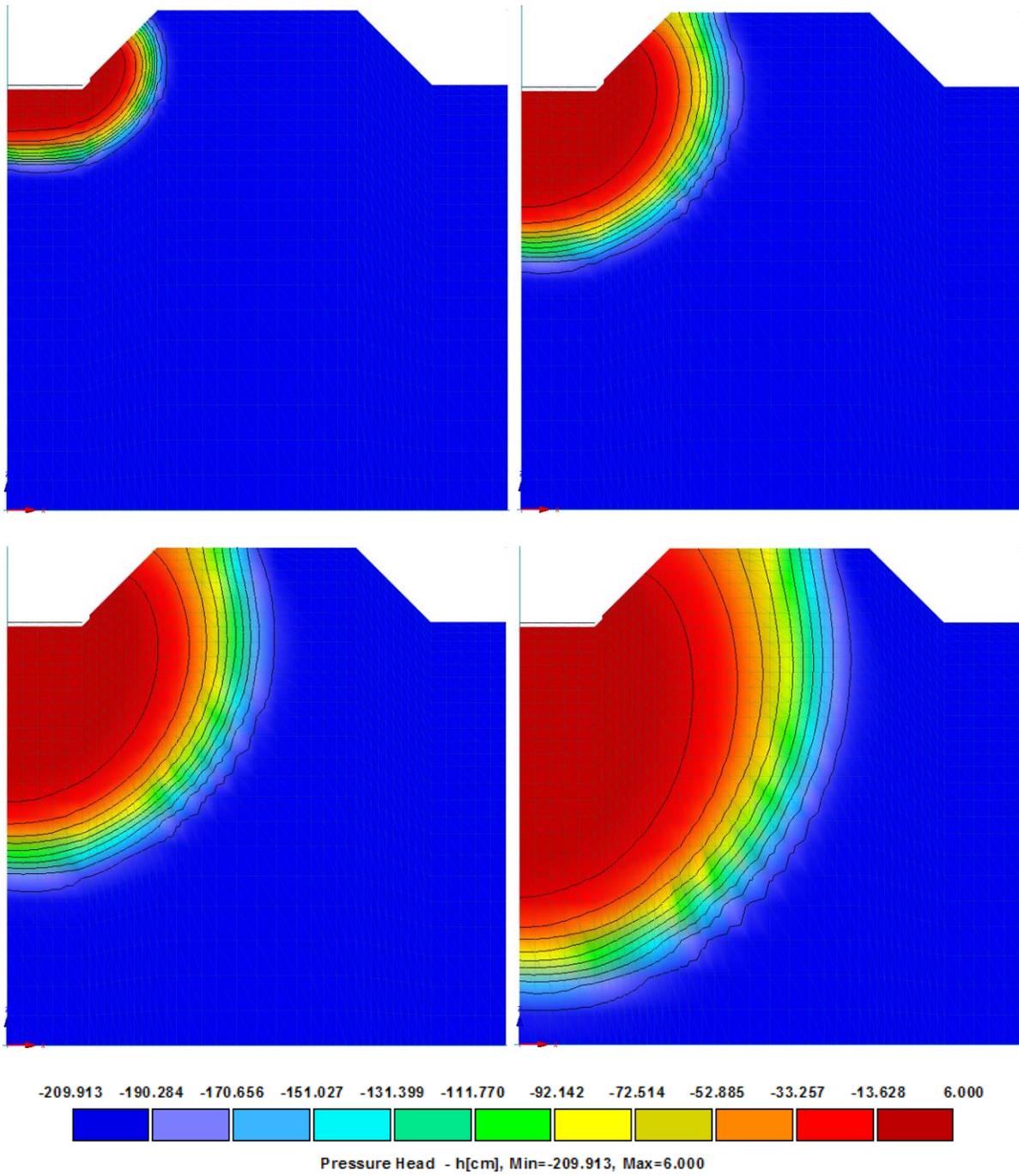


Figure 7.7. Pressure head (cm) profiles at times: a) 0.1, b) 0.5, c) 1, and d) 2 days for example 2.

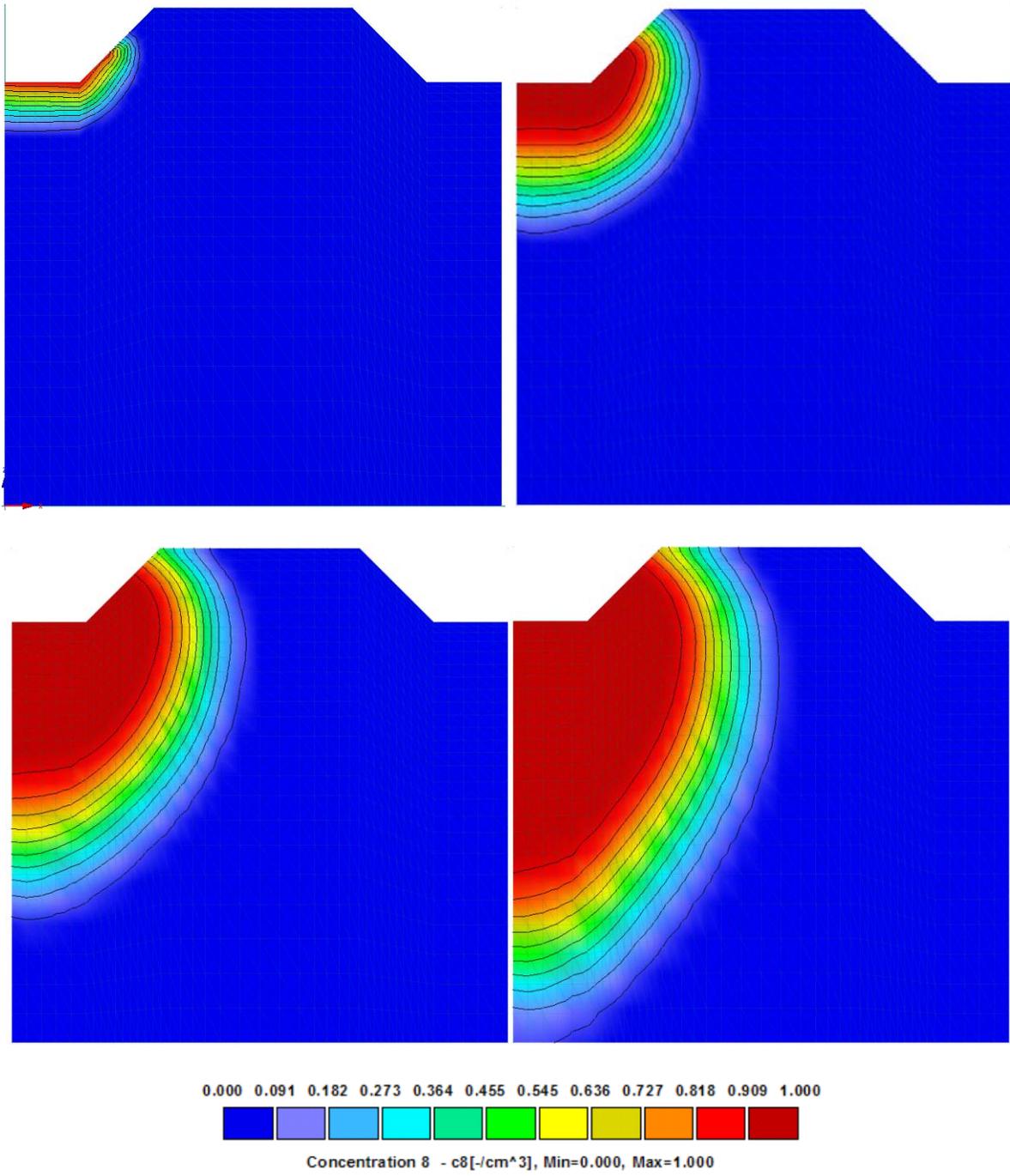


Figure 7.8. Tracer concentration (-) profiles at times: a) 0.1, b) 1, c) 3, and d) 5 days for example 2.

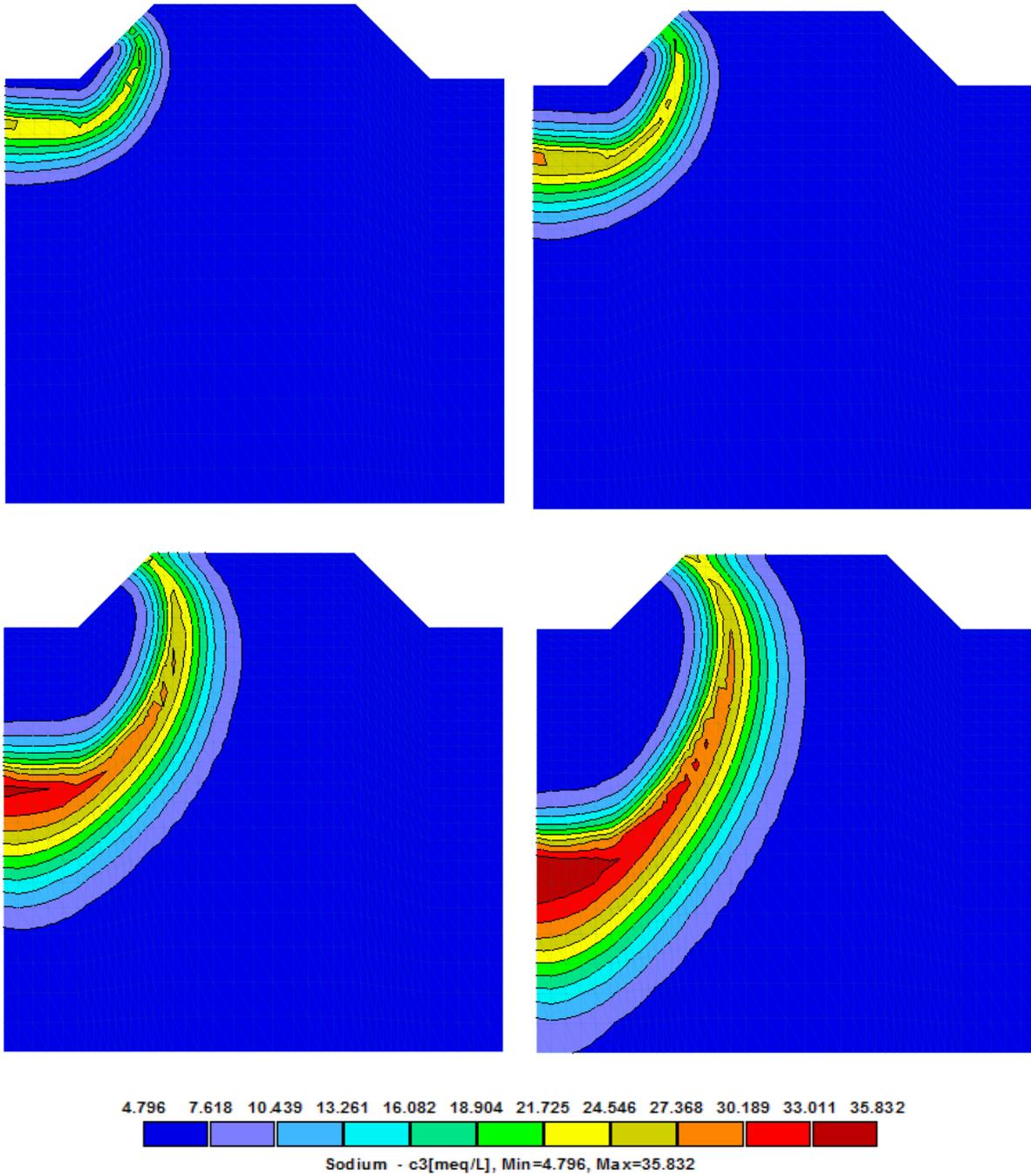


Figure 7.9. Sodium concentration ($\text{mmol}_e\text{L}^{-1}$) profiles at times: a) 0.5, b) 1, c) 3, and d) 5 days for example 2.

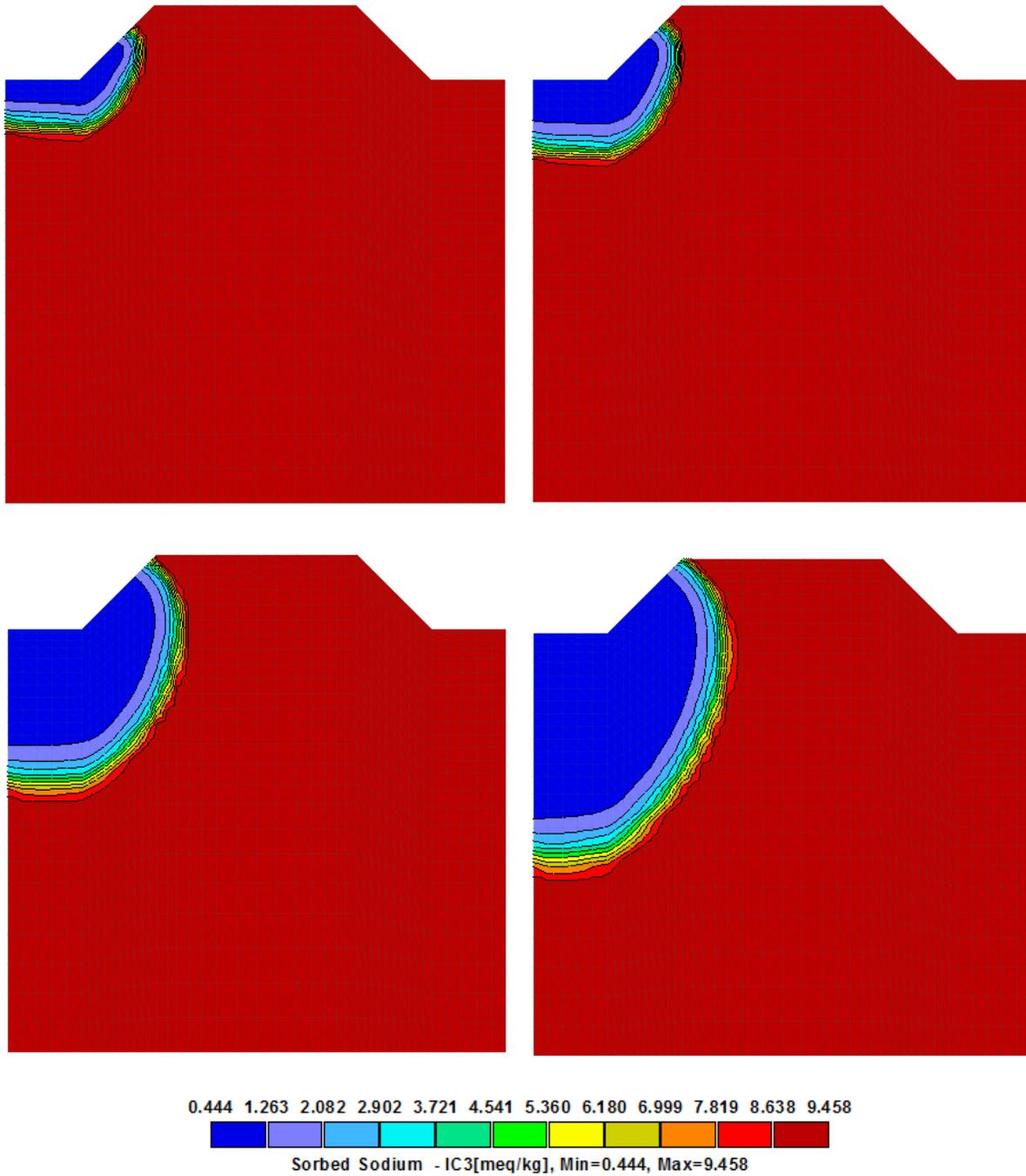


Figure 7.10. Exchangeable concentrations of sodium ($\text{mmol}_c\text{kg}^{-1}$) profiles at times: a) 0.5, b) 1, c) 3, and d) 5 days for example 2.

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