

HP2/3: Extensions of the HP1 Reactive Transport Code to Two and Three Dimensions

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Abstract

A large number of interacting physical, chemical, and biological processes determine the fate of major cations and anions, contaminants (e.g., heavy metals, pesticides), and colloids in soil systems. Also, modeling of soil CO₂ sequestration requires consideration of water flow, heat transport, gas diffusion, and microbiological soil respiration processes. The HP1 simulator (Jacques et al., 2008) is a state-of-the-art model that was specifically developed to evaluate these and similar processes in the unsaturated zone. HP1 couples the one-dimensional variably-saturated flow and transport model HYDRUS-1D (Šimůnek et al., 2008) with the generic geochemical model PHREEQC (Parkhurst and Appelo, 1999). Although HP1 is a versatile code for implementing different geochemical and transport conceptual models in variably-saturated porous media, one of its main limitations is that flow and transport is restricted to one dimension. However, there are many applications that require consideration of various processes in either two- or three-dimensions. Typical examples are flow and transport in soil systems with tiled drains, or with drip and furrow irrigation, or in sloped, layered or heterogeneous systems. Therefore, PHREEQC has recently been coupled also with HYDRUS (2D/3D) (Šimůnek et al., 2011) to handle flow and transport problems, which require a higher dimensionality (HP2/3), and this manuscript describes the capabilities of this new tool. Typical two-dimensional flow and transport problems illustrating the capability of the HP2 simulator are presented in this manuscript. The HP2/3 code uses the graphical user interface of HYDRUS (2D/3D) (Šejna et al., 2011) for input and output processing, enabling definitions and finite element discretization of very complex flow domains.

1. Introduction

The one-dimensional program **HP1**, which couples the **PHREEQC** geochemical code (Parkhurst and Appelo 1999) with **HYDRUS-1D**, was first released in 2005 (Jacques and Šimůnek 2005). This comprehensive simulation tool (HP1 is an acronym for HYDRUS-PHREEQC-1D) can simulate (1) transient water flow, (2) the transport of multiple components, (3) mixed equilibrium/kinetic biogeochemical reactions, and (4) heat transport in one-dimensional variably-saturated porous media (soils). The code uses the Richards equation for simulating one-dimensional variably-saturated water flow and advection-dispersion type equations for heat and solute transport. However, the loosely coupled program can also simulate a broad range of low-temperature biogeochemical reactions in water, the vadose zone and in ground water systems, including interactions with minerals, gases, exchangers and sorption surfaces based on thermodynamic equilibrium, kinetic, or mixed equilibrium-kinetic reactions. HP1 uses the operator-splitting approach with no iterations during one time step (a non-iterative sequential modeling approach).

Jacques and Šimůnek (2005), and Šimůnek et al. (2006), and Jacques et al. (2008ab, 2013), demonstrated the versatility of HP1 in several examples, which included a) the transport of heavy metals (Zn^{2+} , Pb^{2+} , and Cd^{2+}) subject to multiple cation exchange reactions, b) transport with mineral dissolution of amorphous SiO_2 and gibbsite ($\text{Al}(\text{OH})_3$), c) heavy metal transport in a medium with a pH-dependent cation exchange complex, d) infiltration of a hyperalkaline solution in a clay sample (this example considers kinetic precipitation-dissolution of kaolinite, illite, quartz, calcite, dolomite, gypsum, hydrotalcite, and sepiolite), e) long-term transient flow and transport of major cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) and heavy metals (Cd^{2+} , Zn^{2+} , and Pb^{2+}) in a soil profile, f) cadmium leaching in acid sandy soils, g) radionuclide transport, and h) long term uranium migration in agricultural field soils following mineral P-fertilization.

Although HP1 is a versatile code for implementing different geochemical and transport conceptual models in variably-saturated porous media, one of its main limitations is that flow and transport is restricted to one dimension. However, there are many applications, such as flow and transport in soil systems with tiled drains, or with drip and furrow irrigation, or in sloped, layered or heterogeneous systems, that require consideration of various processes in either two- or three-dimensions. Therefore, **PHREEQC** has recently been coupled also with **HYDRUS (2D/3D)** (Šimůnek et al., 2011) to handle flow and transport problems, which require a higher dimensionality (**HP2/3**), and this manuscript describes the capabilities of this new tool.

HP2/3 have, apart from the dimensionality (2D or 3D, respectively), the same capabilities as HP1. The HP2/3 module may be used to analyze water flow, solute movement, and biogeochemical reactions in unsaturated, partially-saturated, or fully saturated two- and three-dimensional porous media. HP2/3 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 HP2/3 code uses the graphical user interface of HYDRUS (2D/3D) (Šejna et al., 2011) for input and output processing, enabling definitions and finite element discretization of very complex flow domains. Typical two-dimensional flow and transport problems illustrating the capability of the HP2 simulator are presented in this manuscript.

2. HYDRUS (2D/3D) Graphical User Interface for HP2/3

The HP2 code is fully incorporated into the HYDRUS (2D/3D) software package, and hence is installed automatically, together with selected examples, when one obtains HYDRUS (2D/3D) and HP2 licenses and downloads HYDRUS from the Hydrus website. Here, we focus mostly on the implementation of the HP2 module into HYDRUS (2D/3D). We will not discuss processes that are related to geometry design, finite element discretization, variably-saturated water flow, heat transport, solute transport, or initial and boundary conditions, which are described in detail in the HYDRUS (2D/3D) documentation (Šimůnek et al., 2011; Šejna et al., 2011). Nor will we discuss

processes and reactions related to biogeochemical reactions that are described in detail in the PHREEQC (Parkhurst and Apello, 1998) and HP1 (Jacques and Šimůnek, 2005, 2010) manuals.

2.1. Common Features with HP1

Similarly as HP1, the HP2 module is activated in the "Main Processes" window by selecting the "Solute Transport" check box and the "HP2 (Hydrus + Phreeqc)" radio button. The number of "Components" is again selected in the "Solute Transport - General Information" window. Large parts of this window (e.g., iteration criteria) are disabled, since they are not relevant to HP2 applications. Also the "HP2/3 Components and Database Pathway" window, in which users have to select the thermodynamic database to be used with HP2 calculations and to list all main components, is the same as in HP1.

2.2. HP2/3 Definitions Window

The main difference between HP1 and HP2 is in how PHREEQC-related inputs (i.e., those that are printed into the PHREEQC.IN input file) are handled. The "HP2/3 Definitions" window has been completely rewritten and reorganized. While in HP1, we had one "HP1 Definitions" window with four external text editors (Fig. 1), in HP2/3, the external text editors were converted into four Internal pages (Fig. 2) (1 - Additions to Thermodynamic Database, 2 - Definitions of Solution Compositions, 3 - Geochemical Model, and 4 - Addition Output), which can all be viewed directly in the "HP2/3 Definitions" window. One additional Page (5 - Database Viewer), in which one can view the selected thermodynamic database, has been added. The five pages can be selected in the top left corner ("List of Pages") of the "HP2/3 Definition" window (Fig. 2).

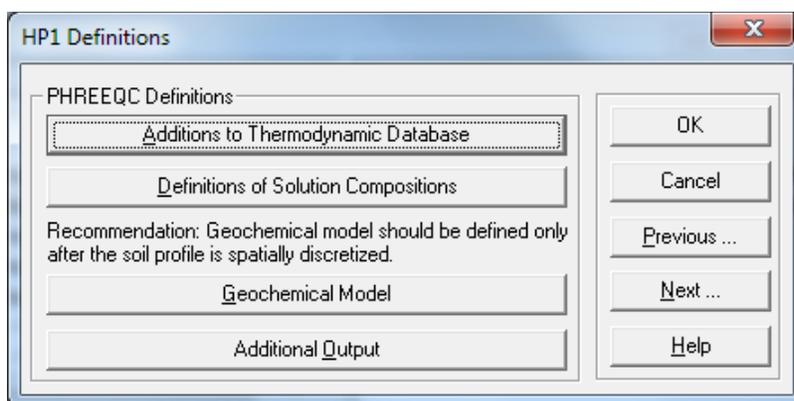


Figure 1. HP1 Definitions window with four external edit windows.

This allowed us to include a section called, "Keywords (double-click to insert)" (bottom left part), which offers the most commonly used PHREEQC Keywords that are used in the first four PHREEQC Pages. The Keywords are hierarchically organized in a tree-like structure in seven main groups: *Solution Definition*, *Geochemical Model*, *Output*, *Chemical/Physical Reaction*, *Database*, *Advanced*, and *Miscellaneous*. A single click opens a particular tree subsection and a double click copies the selected keyword to the Editor Window. This arrangement should dramatically simplify the work of HP2/3 users, and prevent many common errors that they may

have made with HP1. Note the most commonly used Solution Keywords in Figure 2 below - *density*, *-isotope*, *-pe*, *-pH*, *-redox*, *-temperature*, *-units*, and *-water*.

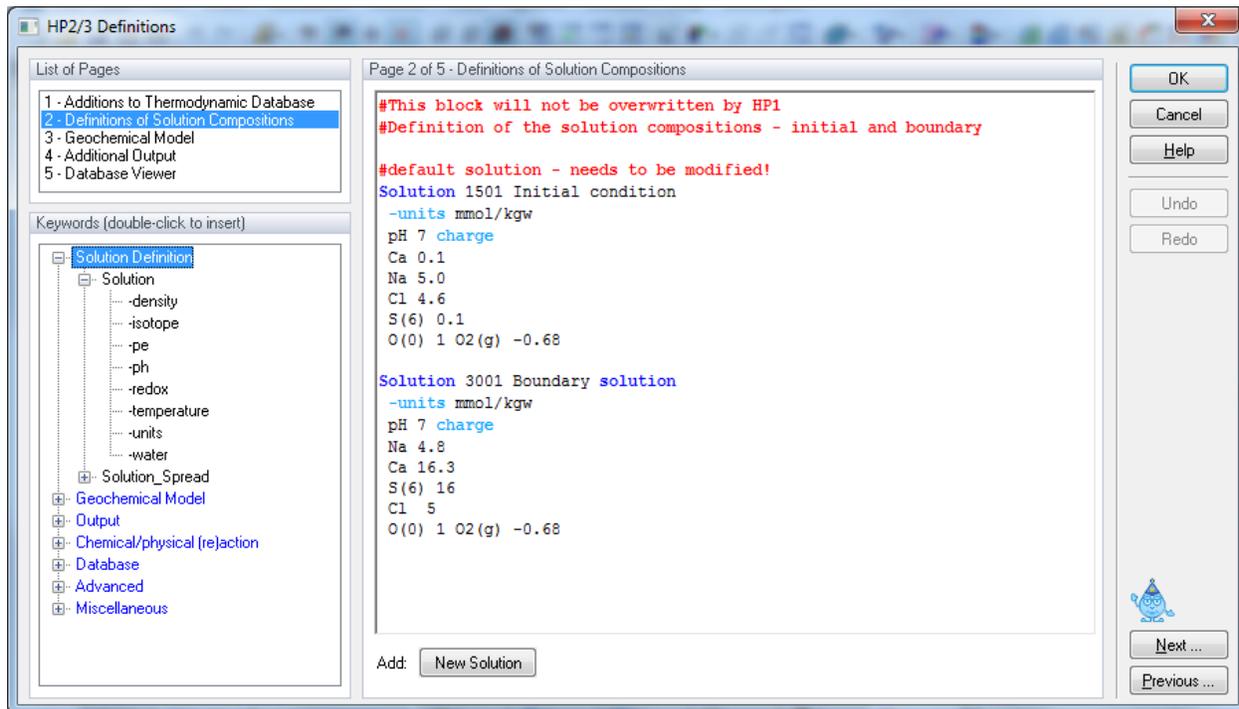


Figure 2. HP2/3 Definitions window with an open page Definitions of Solution Compositions.

Additional new commands were included below the Editor window. For example, the "New Solution" appears below the "Definitions of Solution Compositions" page in Fig. 2. Clicking this command will result in including a template for a new solution (Fig. 3). This solution will have a temperature of 25°C, a pH of 7, be in equilibrium with the atmospheric content of oxygen and have zero concentrations of Ca^{2+} and Cl^- .

```

solution 1001
-temp 25
-units mmol/kgw
-pH 7 charge
Ca 0
Cl 0
O(0) 1 O2(g) -0.68

```

Figure 3. A template for a New Solution.

Similar commands (e.g., *Add Exchange*, *Surface*, *Equilibrium Phases*, and *Kinetics*) appear below the "Geochemical Model" page. These commands can be used to include templates for defining cation exchange, surface complexation, and precipitation/dissolution reactions. For more details about the HP2/3 related GUI, see the HP2 Manual (Šimůnek et al., 2012a).

2.3. HP2/3 Output

The output for the HP2 module is similar to the output for the standard HYDRUS module and for standard variables, such as pressure head, water contents, and so on. Multiple variables can be displayed in the View window (Figure 4). Main components defined in the "HP2/3 Components and Database Pathway" window, variables selected in the "HP2 Print and Punch Controls" window, and variables specified in the "Additional Output" page of the "HP2/3 Definitions" window (Fig. 2) can be displayed this way.

Figure 4 below shows the "Results - Graphical Display" part of the Data Tab of the Navigator Bar for the *Leaching of the Uranium Tailings* example given below (Section 3.2). From the HP2 variables, the first seven are the main components (Total_H, Total_O, Ca, C, U, P, S, and Fe) defined in the "HP2/3 Components and Database Pathway" window, the next two (pH and pe) are variables selected in the "HP2 Print and Punch Controls" window, and finally the last four (calcite, gypsum, ratherfordine and siderite) are mineral phases specified in the "Additional Output" page of the "HP2/3 Definitions" window.

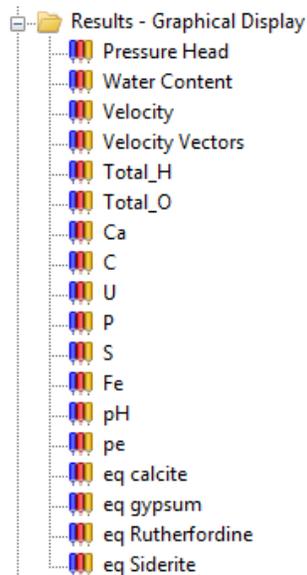


Figure 4. The "Results - Graphical Display" part of the Data Tab of the Navigator Bar for the HP2 module.

3. Example Problems with HP2

Most of the HP1 examples discussed above in the Introduction and provided with the HP1 installation have been rerun using HP2 to verify correct implementation of various components of the coupled program. Two additional two-dimensional examples are discussed below. All of these examples can be downloaded from the HYDRUS/HP2 website (the links are provided below).

3.1. Furrow Irrigation with Cation Exchange

A furrow irrigation problem, similar to the one used in the UNSATCHEM manual (Šimůnek et al., 2012b), was used to simulate two-dimensional infiltration of gypsum saturated water into a sodic soil. The example thus simulates a sodic soil reclamation problem and demonstrates the cation exchange feature of HP2. The schematic representation of the flow domain for the considered furrow irrigation is presented in Figure 5, together with the finite element mesh. 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 for silt are used.

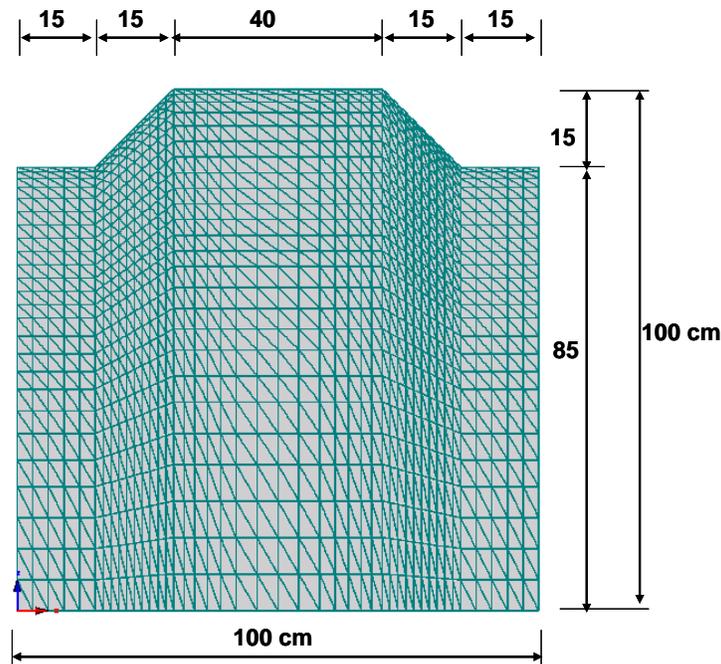


Figure 5. Schematic representation and finite element mesh of the flow domain for the furrow irrigation system.

The calculation was run at a constant temperature of 25 °C. 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=1.0 Mg_T=0.0, Na_T=5.0, K_T=0.0, SO_{4T}=3.5, Cl_T=0.0 mmol L⁻¹. The cation exchange capacity is equal to 7.143 mmol kg⁻¹ (10 mmol dm⁻³) and is divided between exchangeable calcium and sodium (it is equilibrated with the solution). The solution composition of the irrigation water was almost gypsum saturated: Ca_T=16.3, Mg_T=0.0, Na_T=4.4, K_T=0.0, Cl_T=5.0, SO_{4T}=16.0 mmolL⁻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 6 below presents the exchangeable concentrations of sodium to demonstrate typical output of HP2. The exchange phase concentrations reflect the changes in aqueous Na and Ca concentrations.

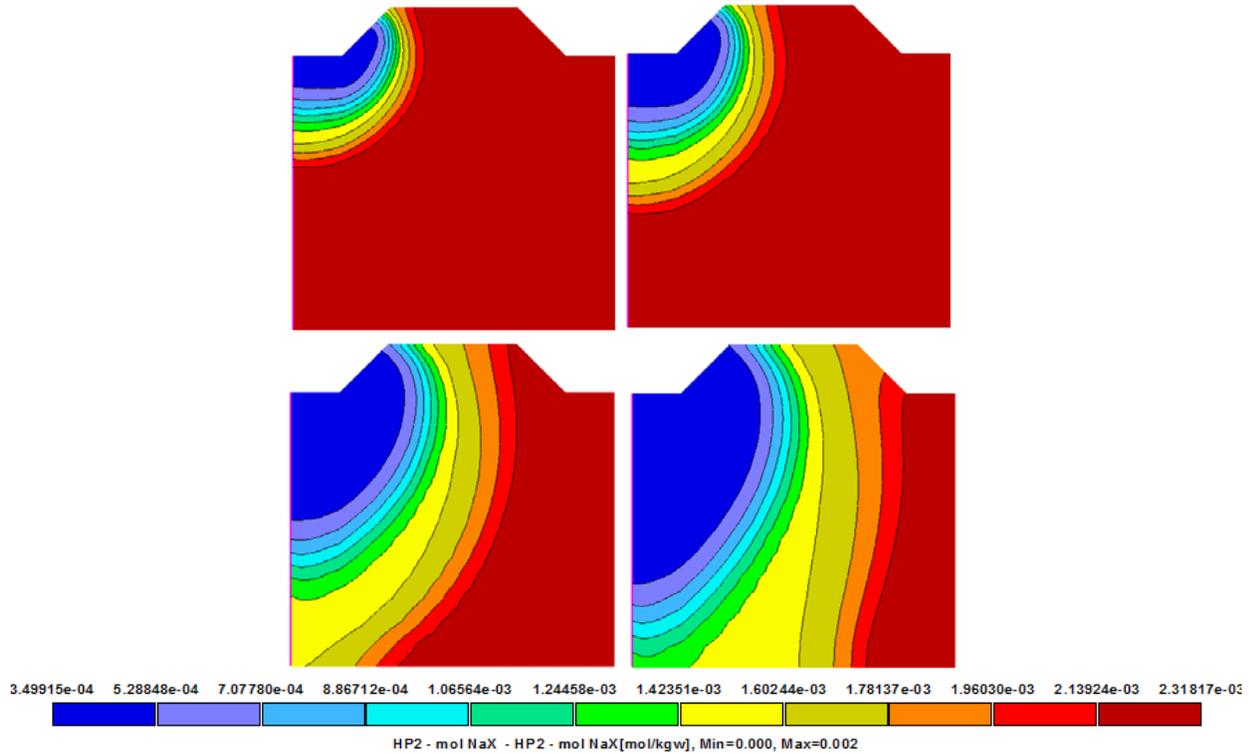


Figure 6. Exchangeable concentrations of sodium (mol kg^{-1}) profiles at times: a) 0.5, b) 1, c) 3, and d) 5 days.

3.2. Leaching of the Uranium Tailings

This problem was inspired by one reported by Yeh and Tripathi (1991), and we have modified it to make it more realistic. The problem considers the release and migration of uranium from a simplified uranium mill tailings pile towards a river. The schematic of the transport domain is shown in Figure 7. The mill tailings pile is located adjacent to a surface that slopes down to a river. The medium has the hydraulic properties of a loam with the saturated hydraulic conductivity of $K_s = 3.78 \text{ m/day}$.

The horizontal bottom of the region is impermeable. The vertical left edge has the Dirichlet boundary condition with a groundwater table 12 m above the bottom of the transport domain (exactly in the middle of the boundary). The top boundary (except for the mill tailing pile and the river) has a flux boundary condition with a net rainfall rate of 0.139 cm/day. The horizontal region on the top of the mill tailings pile is a Cauchy flow boundary with an infiltration rate of 1.39 cm/day. The nodes on the vertical line on the right side and the nodes on the river bottom

have the Dirichlet boundary condition reflecting the position of water in the river (4.5 m above the bottom of the transport domain). A hypothetical pumping well with a withdrawal rate of 271.58 cm²/day is located at (x, z) = (400, 100). The region is discretized using a structured FE mesh with 1564 elements and 852 nodes.

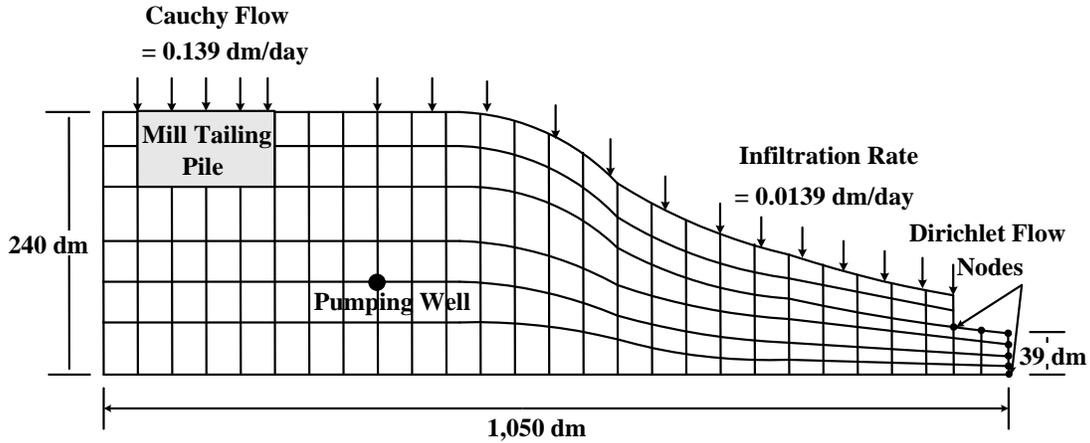


Figure 7. Problem description for the Uranium Tailing Problem (Yeh and Tripathi, 1991).

Chemical Reactions (35 Aqueous Complexation Reactions):

CaCO_{3(aq)}, CaHCO₃⁺, CaSO_{4(aq)}, CaH₂PO₄⁺, CaPO₄⁻, CaHPO₄^(aq), CaOH⁺, FeSO₄^(aq), FeOH⁺, Fe(OH)₂^(aq), Fe(OH)₃⁻, Fe(OH)₄²⁻, (UO₂)(OH)⁺, (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₄²⁺, (UO₂)₃(OH)₅⁺, (UO₂)₄(OH)₇⁺, (UO₂)₃(OH)₇⁻, (UO₂)(CO₃)^(aq), (UO₂)(CO₃)₂²⁻, (UO₂)(CO₃)₃⁴⁻, (UO₂)₂(CO₃)(OH)₃⁻, (UO₂)(SO₄)^(aq), (UO₂)(SO₄)₂²⁻, H₂(UO₂)(PO₄)⁺, H₃(UO₂)(PO₄)²⁺, CaH₄(UO₂)(PO₄)₂²⁺, CaH₅(UO₂)(PO₄)₂³⁺, HCO₃⁻, H₂CO_{3(aq)}, HSO₄⁻, HPO₄²⁻, H₂PO₄⁻, and H₃PO₄

and Precipitation-Dissolution Reactions (14):

CaSO_{4(s)}, CaCO_{3(s)}, Ca₅(OH)(PO₄)_{3(s)}, FeCO_{3(s)}, Ca(UO₂)₂(PO₄)_{2(s)}, Ca₄H(PO₄)_{3(s)}, CaH(PO₄)_(s), Ca(OH)_{2(s)}, Fe₃(PO₄)_{2(s)}, Fe(OH)_{2(s)}, (UO₂)(OH)_{2(s)}, (UO₂)(CO₃)_(s), Fe(UO₂)₂(PO₄)_{2(s)}, and H(UO₂)(PO₄)_(s)

and their thermodynamic equilibrium constants considered in this example are listed in Table 3 of the HP2 manual. For reactive hydrogeochemical transport, the problem consists of eight components: Total H, Total O, Ca, C, uranium, sulfate, phosphate, and Fe. A total of 35 species and 14 minerals is defined for the problem; redox reactions were not considered. Table 1 lists concentrations of the tailing and recharge waters.

Table 1. Initial and boundary compositions of recharge water and pore water in the tailings and regions outside of the tailing for the uranium tailing problem.

Species	Inside the Tailing	Outside the Tailing	Recharge Water
Ca ²⁺	1.0 x 10 ⁻²	1.0 x 10 ⁻²	1.0 x 10 ⁻³
CO ₃ ²⁻	1.0 x 10 ⁻²	1.5 x 10 ⁻³	1.5 x 10 ⁻³
UO ₂ ²⁺	5.0 x 10 ⁻⁴	1.0 x 10 ⁻⁷	1.0 x 10 ⁻⁸
PO ₄ ³⁻	1.0 x 10 ⁻⁶	1.0 x 10 ⁻⁶	1.0 x 10 ⁻⁶
SO ₄ ²⁻	2.0 x 10 ⁻¹	2.0 x 10 ⁻²	1.0 x 10 ⁻⁴
H ⁺	2.0 x 10 ⁻¹	1.0 x 10 ⁻³	1.0 x 10 ⁻³
Fe ²⁺	3.5 x 10 ⁻²	1.0 x 10 ⁻⁷	1.0 x 10 ⁻⁷

The steady-state pressure heads and velocity fields are depicted in Figure 8. Uranium concentration profiles are shown in Figure 9. pH, calcite, and gypsum profiles are shown in Figure 10.

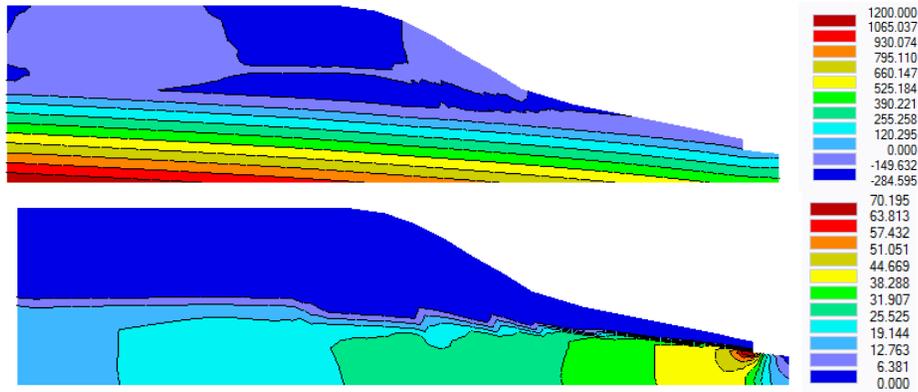


Figure 8. The steady-state pressure head (cm) (top) and flux (cm/d) (bottom) profiles for the Tailing Pile Leaching example.

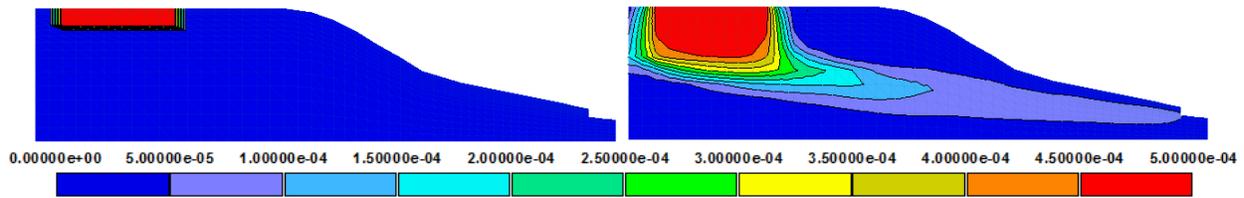


Figure 9. Uranium concentration profiles at time 0 (left), and 500 (right) d for the Tailing Pile Leaching example.

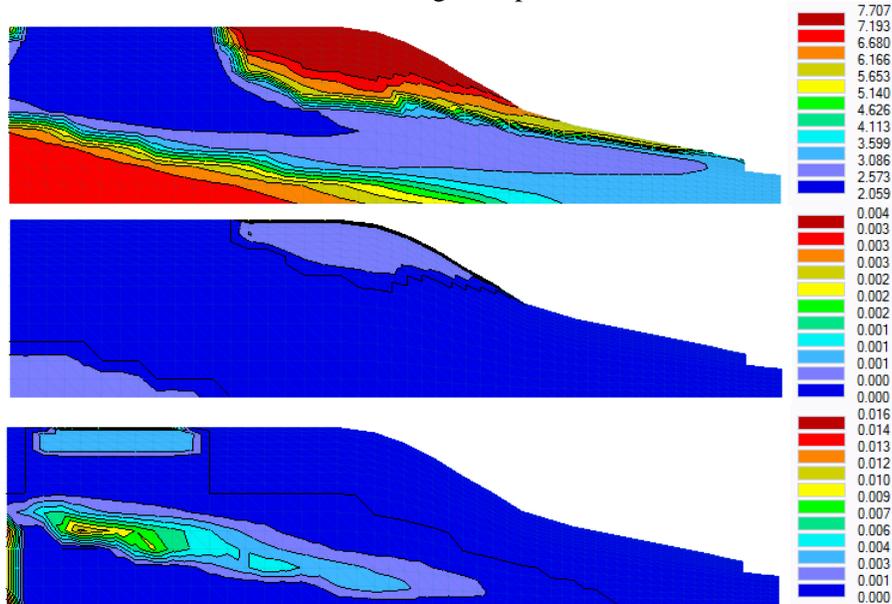


Figure 10. pH (top), calcite (mol/L) (middle), and gypsum (mol/L) (bottom) profiles after 1000 d for the Tailing Pile Leaching example.

4. Important Links

<http://www.pc-progress.com/en/Default.aspx?h3d2-HP2>: web page providing brief description of the HP2 module and listing all main documents (reports and manuscripts) related to this module.

<http://www.pc-progress.com/en/Default.aspx?H3D2-lib-HP2>: Examples demonstrating the HP2 program using one-dimensional (for comparison with HP1) and two-dimensional (those discussed above) problems.

http://www.pc-progress.com/Documents/HYDRUS3D_HP2_Manual.pdf: HP2 manual.

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