Example Problem 5
Formation of residual NAPL saturation in unsaturated porous media

Abstract: *The user is introduced to NAPL flow in porous media. The example problem demonstrates how residual NAPL saturation formation in the unsaturated zone affects NAPL flow. Residual saturation formation in the vadose zone is a process that is often ignored in multi-fluid flow simulators. The user will simulate an actual column experiment and evaluate the impact of residual NAPL saturation on fluid flow. The Water-Oil mode (STOMP-WO) is used for this application.*

5.1 Problem Description

Groundwater contamination as a result of subsurface leakage or surface spills of immiscible organic liquids, such as solvents and hydrocarbon products, is a widespread problem in the industrialized world. Many organic liquids existing as a separate phase are in fact often slightly miscible with water and their solubility often exceeds the drinking water standards by orders of magnitude. To accurately describe the movement of such liquids in the subsurface, separate Nonaqueous Phase Liquid (NAPL), aqueous, and, in the case of volatile organic liquids, gas phase flow has to be considered.

Descriptions of mobile and entrapped NAPL behavior are standard features of multifluid flow simulators. However, these models do not generally incorporate retention of nonaqueous phase liquid (NAPL) in the vadose zone following NAPL imbibition events (e.g., surface spills, tank leaks). Commonly used constitutive relations assume a nonzero NAPL relative permeability when the non-trapped NAPL saturation is greater than zero. As a result, the non-trapped NAPL is allowed to drain from the pore spaces. As NAPL retained in the vadose zone can serve as a long-term source for groundwater contamination, via transport through the gas or aqueous phase, understanding and predicting the processes of residual NAPL formation and remobilization is critical when considering restoration or management of a contaminated subsurface site. A theory describing the formation of residual NAPL saturation (Lenhard et al., 2003) has recently been implemented into the simulator. Simulation results have been compared to experimental data (White et al, 2003).

The theory of Lenhard et al. (2003) recognizes residual NAPL formation within the pore-space region between the apparent aqueous saturation and the maximum apparent total-liquid saturation. This theory is based on fluid displacement physics in pore spaces. The Lenhard et al. model (2003) allows for residual NAPL collocated with mobile NAPL, which can reduce the mobile NAPL relative permeability. Ignoring air entrapment by NAPL, the effective residual NAPL saturation, $\bar{S}_{nr}$, is computed as

$$\bar{S}_{nr} = \bar{S}_{nr}^{max} \left(\bar{\bar{S}}_t^{max} - \bar{\bar{S}}_l \right)^{1/2} \left(1 - \bar{\bar{S}}_l \right)^{3/2} \qquad 5.1$$

where $\bar{S}_{nr}^{max}$ is the maximum residual NAPL saturation that can be obtained in a porous medium, $\bar{\bar{S}}_l$ is the apparent aqueous phase saturation, and $\bar{\bar{S}}_t^{max}$ is the historic maximum apparent total-liquid saturation. The first and second terms between brackets are factors related to the volume of pore space occupied by NAPL, and the size of the pore containing the NAPL, respectively. The reader is referred to Lenhard et al. (2003) for a detailed description and derivation of 5.1.

The Soltrol®220 experiment was conducted in a 1-m-long column with a 5.0 cm inside diameter. The column was packed under saturated conditions with 90 cm of a medium-grained Hanford sand. Denoting the bottom as z = 0 cm, the column was calibrated for dual-energy gamma radiation measured at nine locations: z = 5, 15, 25, 35, 45, 55, 65, 75, and 85 cm. The column was subsequently drained at a rate of 10 cm/hr from z = 90 cm to z = 20 cm after which the porous medium system was allowed to reach quasi-static equilibrium by waiting seven days. After this period, 120 ml Soltrol®220 was injected at a rate of 1 ml/min for

120 minutes. After the injection, the LNAPL was allowed to infiltrate and redistribute. The column was scanned daily for the duration of the experiment (50 days) to determine LNAPL and water saturations. The fluid properties and hydraulic properties of the porous medium, including the maximum entrapped Soltrol®220 saturation, $\bar{S}_{ne}^{\max}$, were obtained in independent procedures.

The Soltrol® 220 imbibition experiment was modeled, starting with a drained column (i.e., hydrostatic aqueous phase), with the water table set at 20.0 cm above the column bottom and injecting 120 ml of NAPL over a 2-hour period in the top grid cell. The experiment was simulated over a 50-day period, with time steps limited to 0.5 hr for the first 100 hrs and 4.0 hr for the remaining period. During the first 7-hr period time stepping is limited by the convergence capabilities of the Newton-Raphson linearization scheme. The time step is cut to 20% of its previous value if a converged solution to the coupled nonlinear equations is not found. Beyond the first 7-hr period, time stepping is controlled by the specified limits. The input files for STOMP modes with NAPL include the Oil Properties Card and the NAPL Relative Permeability Card. Boundary conditions for this phase have to specified in the Boundary Conditions Card. Results of simulations with and without the formation of residual saturation are compared with experimental results in Figures 5.1, 5.2, and 5.3.

References

Lenhard, RJ, et al. 2004, "A Constitutive Model for Air-Napl-Water Flow in the Vadose Zone Accounting for Immobile, Non-Occluded (Residual) Napl in Strongly Water-Wet Porous Media." *Journal of Contaminant Hydrology* 73:283-304.

M D White, M Oostrom, and R J Lenhard. "A Practical Model for Mobile, Residual, and Entrapped NAPL in Water-Wet Porous Media. " Ground Water 42.5 (2004): 734-746.

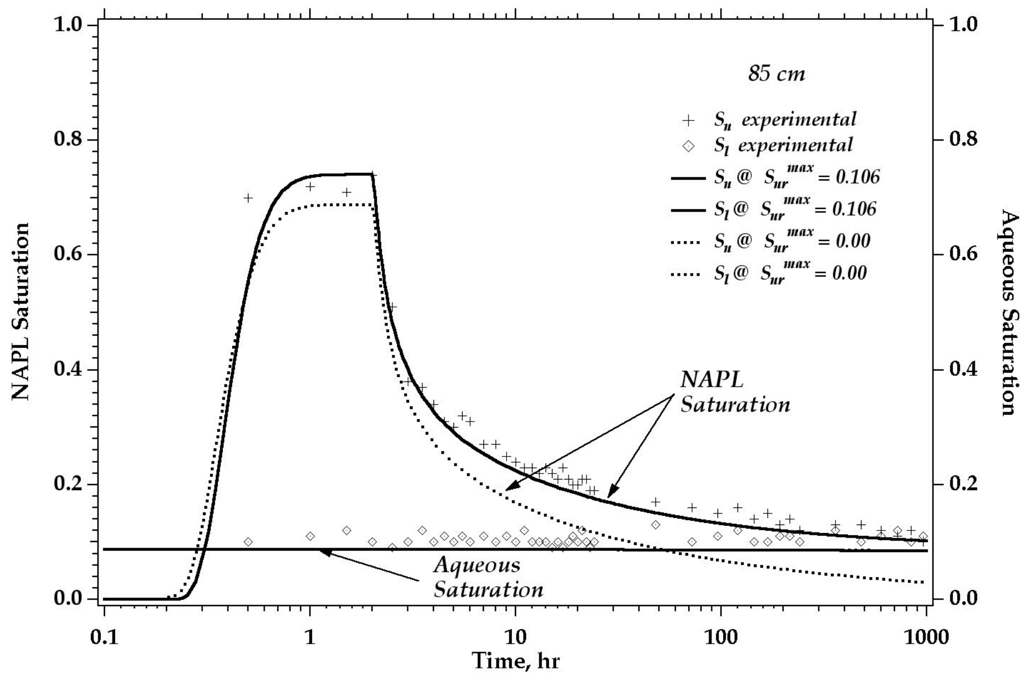

Figure 5.1 Comparison of aqueous and NAPL saturation between laboratory observations and numerical simulations at z = 85 cm for the Soltrol® 220 infiltration experiment.

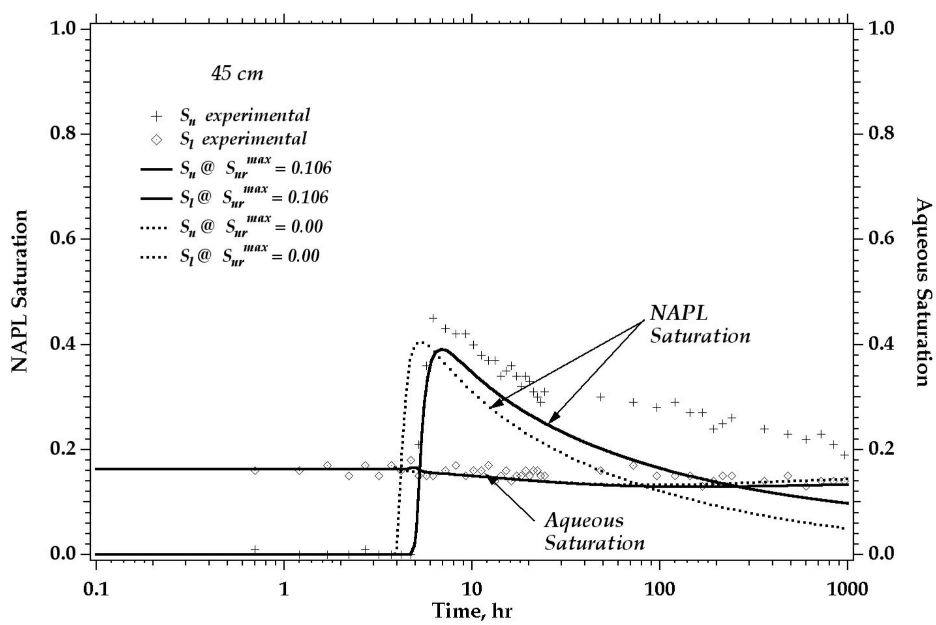

Figure 5.2 Comparison of aqueous and NAPL saturation between laboratory observations and numerical simulations z = 45 cm for the Soltrol® 220 infiltration experiment.

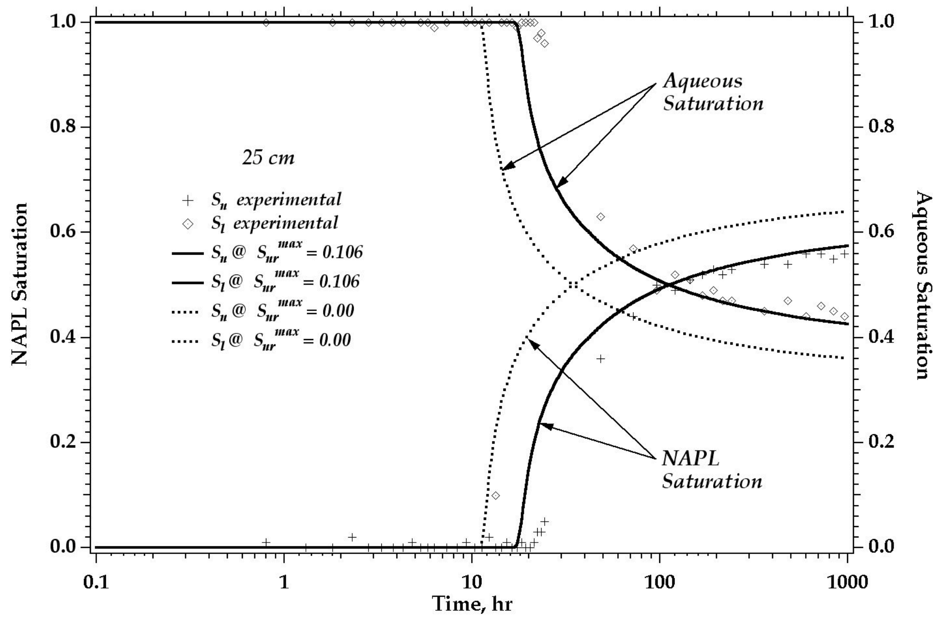

Figure 5.3 Comparison of aqueous and NAPL saturation between laboratory observations and numerical simulations at z = 25 cm for the Soltrol® 220 infiltration experiment.

5.2 Exercises

1. The experiment was conducted in a 1D column with a 5-cm diameter. Verify that the Grid Card has been set up properly.
2. Execute the simulation with the input file shown in section 5.3. Plot the NAPL saturation vs. elevation at z = 85, 45, and 25 cm and compare the simulated NAPL saturations with Figs. 5.1, 5.2, and 5.3.
3. The residual formation option is specified in the Saturation Function Card:

```
#-------------------------------------------------------------------
~Saturation Function Card
#-------------------------------------------------------------------
72.0,dynes/cm,38.0,dynes/cm,,,
Sand,Brooks and Corey w/ residual,10.12,cm,2.67,0.08,72.0,dynes/cm,0.106,
```

   With the help of the User's Guide, complete the card for nonhysteretic conditions. Plot the NAPL saturation vs. elevation at z = 85, 45, and 25 cm and compare the simulated NAPL saturations with Figs. 5.1, 5.2, and 5.3.

4. Increase the maximum residual saturation to 0.212. Execute simulation, make plots at z = 85, 45, and 25 cm, and compare with previously obtained results.

5. Compute equivalent Van Genuchten values for this porous medium. Execute simulation, make plots at z = 85, 45, and 25 cm, and compare with previously obtained results.
6. Reduce the permeability by a factor 10. Execute simulation, make plots at z = 85, 45, and 25 cm, and compare with previously obtained results.

5.3 Input File

```
#-------------------------------------------------------------------
~Simulation Title Card
#-------------------------------------------------------------------
1,
STOMP Tutorial Problem 5,
M.Oostrom/Mark White,
Pacific Northwest National Laboratory,
Jan 2003,
3 PM PST,
2,
Soltrol 170 movement in coarse sand,
Testing of new residual saturation formation theory,

#-------------------------------------------------------------------
~Solution Control Card
#-------------------------------------------------------------------
Normal,
Water-Oil,
2,
0,s,100,hr,1,s,0.5,hr,1.25,8,1.e-6,
100,hr,50,d,1,s,4.0,hr,1.25,8,1.e-6,
10000,
Variable Aqueous Diffusion,
0,

#-------------------------------------------------------------------
~Grid Card
#-------------------------------------------------------------------
Cartesian,
1,1,91,
0.0,cm,4.431135,cm,
0.0,cm,4.431135,cm,
0.0,cm,0.5,cm,89@1,cm,90,cm,

#-------------------------------------------------------------------
~Rock/Soil Zonation Card
#-------------------------------------------------------------------
1,
Sand,1,1,1,1,1,91,

#-------------------------------------------------------------------
~Mechanical Properties Card
#-------------------------------------------------------------------
Sand,,kg/m^3,0.36,0.36,,,Millington and Quirk,

#-------------------------------------------------------------------
~Hydraulic Properties Card
#-------------------------------------------------------------------
Sand,,,,,1.41e-11,m^2,

#-------------------------------------------------------------------
~Saturation Function Card
#-------------------------------------------------------------------
72.0,dynes/cm,38.0,dynes/cm,,,
Sand,Brooks and Corey w/ residual,10.12,cm,2.67,0.08,72.0,dynes/cm,0.106,
```

```
#-------------------------------------------------------------------
~Aqueous Relative Permeability Card
#-------------------------------------------------------------------
Sand,Burdine,,

#-------------------------------------------------------------------
~NAPL Relative Permeability Card
#-------------------------------------------------------------------
Sand,Burdine,,

#-------------------------------------------------------------------
~Oil Properties Card
#-------------------------------------------------------------------
Soltrol 220,
153.82,g/mol,250.,K,349.9,K,556.4,K,
45.6,bar,275.9,cm^3/mol,0.272,0.193,0.0,debyes,
4.072e+1,2.0496e-1,-2.27e-4,8.843e-8,
Equation 1,-7.07139,1.71497,-2.89930,-2.49466,
Constant,810,kg/m^3,
Constant,4.5e-3,Pa s,
1.0e10,Pa,

#-------------------------------------------------------------------
~Initial Conditions Card
#-------------------------------------------------------------------
2,
Aqueous Pressure,103259,Pa,,,,,-9793.5192,1/m,1,1,1,1,1,91,
NAPL Pressure,-1.e9,Pa,,,,,,,1,1,1,1,1,91,

#-------------------------------------------------------------------
~Boundary Conditions Card
#-------------------------------------------------------------------
2,
Top,Zero Flux,Neumann,
1,1,1,1,91,91,2,
0,hr,-1.e9,Pa,0.0,-0.05093,cm/min,
2,hr,-1.e9,Pa,0.0,-0.05093,cm/min,
Bottom,Dirichlet,Zero Flux,
1,1,1,1,1,1,1,
0.0,hr,103284,Pa,0.0,101325,Pa,

#-------------------------------------------------------------------
~Output Control Card
#-------------------------------------------------------------------
9,
1,1,86,
1,1,76,
1,1,66,
1,1,56,
1,1,46,
1,1,36,
1,1,26,
1,1,16,
1,1,6,
1,1,hr,cm,6,6,6,
3,
Aqueous Saturation,,
```

```
NAPL Saturation,,
Residual NAPL Saturation,,
0,
3,
Aqueous Saturation,,
NAPL Saturation,,
Residual NAPL Saturation,,

#----------------------------------------------------------------------
~Surface Flux Card
#----------------------------------------------------------------------
3,
NAPL volumetric flux,ml/min,ml,top,1,1,1,1,91,91,
NAPL volumetric flux,ml/min,ml,bottom,1,1,1,1,1,1,
aqueous volumetric flux,ml/min,ml,bottom,1,1,1,1,1,1,
```

5.4 Solutions to Selected Exercises

Exercise 2

Simulated NAPL saturations at z = 25, 45, and 85 cm are shown in Figure 5.4. The results are identical to the solid NAPL lines in Figures 5.1, 5.2, and 5.3.

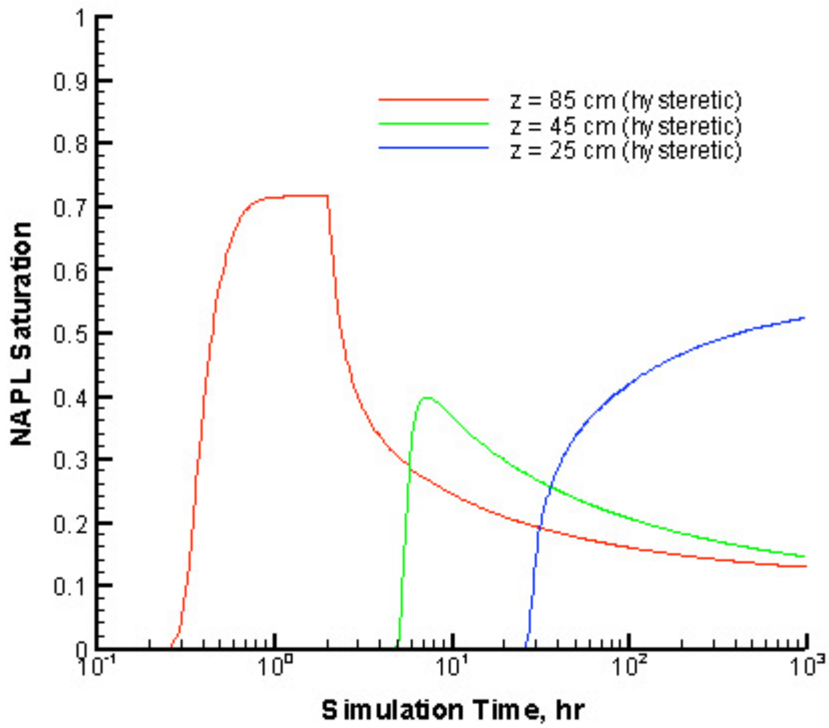

Figure 5.4 Simulated NAPL saturation at z = 85, 45 and 25 cm .

Exercise 3

Simulated NAPL saturations at z = 25, 45, and 85 cm are shown in Figure 5.5. The results for the nonhysteretic simulation are identical to the dashed NAPL lines in Figures 5.1, 5.2, and 5.3. To simulate nonhysteretic conditions use the following Saturation Function Card:

```
#-------------------------------------------------------------------
~Saturation Function Card
#-------------------------------------------------------------------
72.0,dynes/cm,38.0,dynes/cm,,,
Sand, Brooks and Corey,10.12,cm,2.67,0.08,72.0,dynes/cm,
```

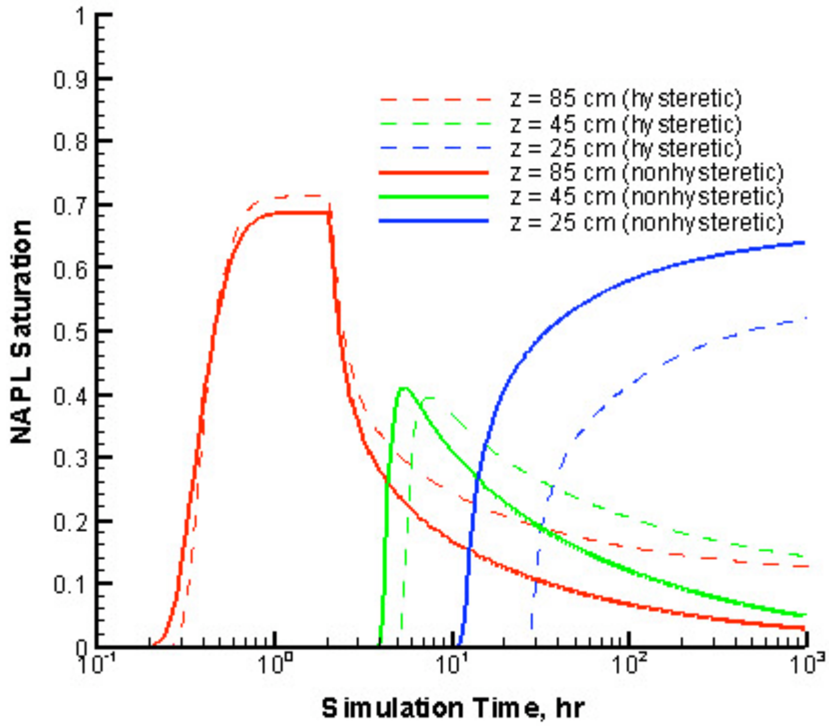

Figure 5.5 A comparison of hysteretic versus nonhysteretic NAPL 1-dimensional infiltration and redistribution.

Exercise 4

The effects of increasing the maximum residual saturation are illustrated in Figure 5.6. As the NAPL descends through the soil column it does not drain as easily and the NAPL saturation does not decline as rapidly as before. Since more NAPL is retained in the upper sections of the column, node 25 (blue line) does not see NAPL appearing until later in the simulation. Increasing the residual maximum saturation to 0.212 requires the following Saturation Function Card.

```
#-------------------------------------------------------------------
~Saturation Function Card
#-------------------------------------------------------------------
72.0,dynes/cm,38.0,dynes/cm,,,
Sand,Brooks and Corey w/Residual,10.12,cm,2.67,0.08,72.0,dynes/cm,.212,
```

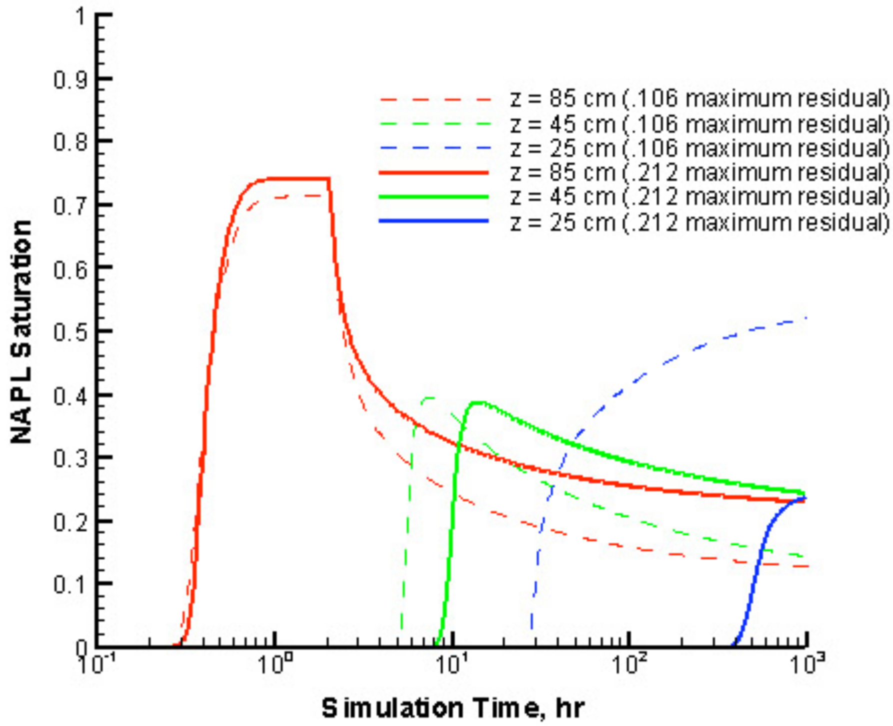

Figure 5.6 The effect of maximum residual saturation on NAPL 1-dimensional infiltration.