LBNL-49375

TMVOC, A Numerical Simulator for Three-Phase Non-isothermal Flows of Multicomponent Hydrocarbon Mixtures in Saturated-Unsaturated Heterogeneous Media

Karsten Pruess and Alfredo Battistelli&*

* Lawrence Berkeley National Laboratory, Berkeley, CA 94720, U.S.A.

& Aquater S.p.A., 61047 San Lorenzo in Campo (PU), Italy

April 2002

This work was supported, in part, by the U.S. Department of Energy through the Office of Basic Energy Sciences under Contract No. DE-AC03-76SF00098. Partial support was also provided by a grant from Aquater S.p.A. (ENI Group) to the Lawrence Berkeley National Laboratory in the frame of the REPIS project sponsored by the ENI Research Fund.

Abstract

TMVOC is a numerical simulator for three-phase non-isothermal flow of water, soil gas, and a multicomponent mixture of volatile organic chemicals (VOCs) in multidimensional heterogeneous porous media. It is an extension of the TOUGH2 general-purpose simulation program developed at the Lawrence Berkeley National Laboratory. TMVOC is designed for applications to contamination problems that involve hydrocarbon fuel or organic solvent spills in saturated and unsaturated zones. It can model contaminant behavior under "natural" environmental conditions, as well as for engineered systems, such as soil vapor extraction, groundwater pumping, or steam-assisted source remediation.

This report is a self-contained guide to applications of TMVOC to subsurface contamination problems involving non-aqueous phase liquids (NAPLs). It gives a technical description of the TMVOC code, including a discussion of the physical processes modeled, and the mathematical and numerical methods used. Detailed instructions for preparing input data are presented along with illustrative sample problems.

TABLE OF CONTENTS

LIST OF FIGURES vii

LIST OF TABLES xi

1. INTRODUCTION 1

2. HARDWARE REQUIREMENTS AND CODE INSTALLATION 3

3. PHYSICAL PROCESSES AND ASSUMPTIONS 5

4. FLUID PROPERTIES 7

- 4.1 Gas Phase 9
- 4.2 Aqueous (Water) Phase 13
- 4.3 Oil (NAPL) Phase 15
- 4.4 Adsorption of VOCs 18
- 4.5 Biodegradation 18

5. IMPLEMENTATION IN TMVOC 19

- 5.1 Scope and Methodology 19
- 5.2 Program Structure and Execution 20

6. TMVOC ARRAY STRUCTURE 23

- 6.1 Primary Thermodynamic Variables 23
- 6.2 Change of Phase Composition 26
- 6.3 Thermophysical Property Arrays 28
- 6.4 Linear Equation Setup 31
- 6.5 Dimensioning of Major Arrays 32

7. PREPARATION OF INPUT DATA 34

- 7.1 TMVOC Input Data 34
- 7.2 Geometry Data 40

8. USER FEATURES 44

- 8.1 Initial Conditions and Restarting 44
- 8.2 Boundary Conditions and “Inactive” Elements 45
- 8.3 Sinks and Sources 47
- 8.4 Heat Exchange with Confining Beds 49
- 8.5 Block-by-block Permeability Modification 51
- 8.6 Linear Equation Solvers 52

9. OUTPUT FROM TMVOC 55

10. SAMPLE PROBLEMS 58

10.1 Problem No. 1 (*r7c*) - Demonstrating Initialization of Different Phase Conditions 60

10.2 Problem No. 2 (*rblm*) - 1-D Buckley-Leverett Flow 63

10.3 Problem No. 3 (*rdif2*) - Diffusion 67

10.4 Problem No. 4 (*rtcem*) - Steam Displacement of a NAPL in a Laboratory Column 71

10.5 Problem No. 5 (*rbt*) - Steam Displacement of a Benzene-Toluene Mixture in a Laboratory Column 85

10.6 Problem No. 6 (*rad*) - Air Displacement of a NAPL from a Laboratory Column 96

10.7 Problem No. 7 (*r2dl*) - NAPL Spill in the Unsaturated Zone 108

11. CONCLUDING REMARKS 127

ACKNOWLEDGEMENT 127

REFERENCES 128

Appendix A. Mass and Energy Balances 133

Appendix B. Space and Time Discretization 136

Appendix C. Description of Flow in Fractured Media 140

Appendix D. Multiphase Diffusion 143

Appendix E. TMVOC Input Formats 148

Appendix F. Input Formats for MESHMAKER 172

Appendix G. Relative Permeability Functions 179

Appendix H. Capillary Pressure Functions 182

SUBJECT INDEX 183

LIST OF FIGURES

Figure 1.1 Example of coding for internal version control 2

Figure 4.1 Phase composition and phase changes considered by TMVOC 7

Figure 5.2.1 Modular architecture of TMVOC 20

Figure 6.3.1 Structure of thermophysical property arrays in TMVOC 28

Figure 6.3.2 Linear equation structure 30

Figure 7.1.1 TMVOC input formats 37

Figure 7.2.1 User options for supplying geometry data 41

Figure 10.1.1 TMVOC input file for initialization test 61

Figure 10.1.2 Portion of printout from initialization test..... 62

Figure 10.2.1 Input file for sample problem 2 (Buckley-Leverett) 64

Figure 10.2.2 Part of printed output for sample problem 2 65

Figure 10.3.1 Input file for sample problem 3 (diffusion) 68

Figure 10.3.2 Part of printed output for sample problem 3 69

Figure 10.4.1 TMVOC input file for part 1 of problem 4 (TCE injection) 74

Figure 10.4.2 Portion of printed output for part 1 of problem 4 75

Figure 10.4.3 Portion of TMVOC input file for part 2 of problem 4 (waterflood) 77

Figure 10.4.4 Portion of printed output for part 2 of problem 4..... 78

Figure 10.4.5 Portion of TMVOC input file for part 3 of problem 4 (TCE injection) 80

Figure 10.4.6 Portion of printed output for part 3 of problem 4 81

Figure 10.4.7. Portion of TMVOC input file for the steamflood in the $O_2 + N_2$ variation of problem 4 83

Figure 10.4.8. Portion of printed output for the steamflood in the $O_2 + N_2$ variation of problem 4 84

Figure 10.5.1 TMVOC input file for part 1 of problem 5 (injection of benzene and toluene into a laboratory column) 87

Figure 10.5.2 Portion of printout of part 1 of problem 5 88

Figure 10.5.3 TMVOC input file for part 2 of problem 5 (waterflood) 89

Figure 10.5.4 Portion of printout of part 2 of problem 5 90

Figure 10.5.5 NAPL bank before waterflood, and after injection of 1.2, 9, and 10.2 pore volumes of water 91

Figure 10.5.6 Benzene and toluene mass fractions at outlet (grid block AA 50) during waterflood 91

Figure 10.5.7 TMVOC input file for part 3 of problem 5 (steamflood) 92

Figure 10.5.8 Portion of printout for part 3 of problem 5 (steamflood) 93

Figure 10.5.9 Calling sequence of program units in part 3 of problem 5 95

Figure 10.6.1 TMVOC input file for part 1 of problem 6 99

Figure 10.6.2 TMVOC input file for part 2 of problem 6 (NAPL injection) 100

Figure 10.6.3 Portion of printed output for part 2 of problem 6 (NAPL injection) 102

Figure 10.6.4 TMVOC input file for part 3 of problem 6 (redistribution) 103

Figure 10.6.5 Portion of printed output for part 3 of problem 6 (redistribution) 104

Figure 10.6.6 TMVOC input file for part 4 of problem 6 (airflooding) 105

Figure 10.6.7 Portion of output file for part 4 of problem X (air flooding) 106

Figure 10.6.8 o-xylene and toluene concentrations in the NAPL phase after 1740 s (29 min) of air flooding 107

Figure 10.6.9 o-xylene and toluene concentrations in the gas phase and NAPL saturation in the uppermost element as a function of time during the air flooding 107

Figure 10.7.1 Conceptual model of 2-D vertical section problem for simulating a multicomponent NAPL spill in the unsaturated zone 108

Figure 10.7.2 MESHMAKER input data for 2-D vertical section grid 109

Figure 10.7.3 Grid diagram for 2-D vertical section model 110

Figure 10.7.4 Portion of TMVOC input file for part 1 of problem 7 (obtaining steady-state conditions prior to NAPL spill) 114

Figure 10.7.5 Portion of printout for part 1 of problem 7 116

Figure 10.7.6 Portion of TMVOC input file for part 2 (NAPL spill) of problem 7 117

Figure 10.7.7 Portion of printout for part 2 (NAPL spill) of problem 7 118

Figure 10.7.8 Contour plot of total VOC mass fraction in the aqueous phase at the end of the NAPL spill period 119

Figure 10.7.9 Portion of TMVOC input file for part 3 (NAPL redistribution) of problem 7.... 120

Figure 10.7.10 Portion of printout for part 3 (NAPL redistribution) of problem 7 121

Figure 10.7.11 Contour plot of total VOC mass fraction in the aqueous phase at the end of the NAPL redistribution period 122

Figure 10.7.12 NAPL saturations at the end of the redistribution period 122

Figure 10.7.13 Portion of TMVOC input file for part 4 (extraction) of problem 7 123

Figure 10.7.14 Portion of printed output for part 4 (extraction) of problem 7 124

Figure 10.7.15 Contour plot of total VOC mass fraction in the aqueous phase at the end of the extraction period 125

Figure 10.7.16 Evolution of NAPL saturation at selected locations, labeled with x, z-values..... 126

Figure 10.7.17 Evolution of VOC mass fractions in aqueous phase at selected locations, labeled with x, z-values 126

Figure B.1 Space discretization and geometry data in the integral finite difference method..... 136

Figure C.1 Idealized double porosity model of a fractured porous medium..... 140

Figure C.2 Subgridding in the method of "multiple interacting continua" (MINC)..... 141

Figure C.3. Flow connections in the “dual permeability” model..... 142

Figure F.1 MESHMaker input formats..... 173

LIST OF TABLES

Table 1. TMVOC program structure 21

Table 2. Labeling of mass components 24

Table 3. Primary thermodynamic variables used by TMVOC 25

Table 4. Summary of major common blocks 33

Table 5. TMVOC input data blocks 35

Table 6. TMVOC disk files 39

Table E.1 Phase identifiers and primary thermodynamic variables used by TMVOC 161

Table E.2 Choice of primary variables in T2VOC 161

1. Introduction

TMVOC is designed for simulating the flow of multicomponent mixtures of volatile organic chemicals (VOCs), such as crude oil, gasoline or diesel, and organic solvents, in variably saturated media. It can be used to analyze the fate and transport of non-aqueous phase liquids (NAPLs) in the vadose zone as well as below the water table. The NAPL may consist of a general multi-component mixture of organic fluids. In addition one or several non-condensible gases may be present. Any and all phase compositions in a gas-water-NAPL system are treated, including single, two-phase, and three-phase conditions. Flows can be non-isothermal, and may involve advective, diffusive, phase-partitioning, and sorptive processes. A simple model for biodegradation is provided as well. Chief applications for which TMVOC is designed include analysis of NAPL spills and remediation alternatives in the vadose zone and below the water table.

TMVOC is implemented as a specialized module in the framework of the general multi-purpose simulator TOUGH2, and it retains the general process capabilities and user features of TOUGH2 (Pruess et al., 1999). The specific methodology used to treat multicomponent VOCs was adapted from Adenekan (1992) and Adenekan et al. (1993). The TMVOC program consists of a number of functional units with flexible and transparent interfaces. Much of what the program units do is spelled out in internal comments and in printed output. TMVOC is distributed along with a number of input data files for sample problems. Besides providing benchmarks for proper code installation, these can serve as a self-teaching tutorial in the use of TMVOC, and they provide templates to help jump-start new applications.

A number of ancillary programs are available to facilitate certain operations that occur in many TMVOC applications. Examples include the assignment of initial and boundary conditions, modification of MESH files, and extracting of graphics files from output data. A selection of "utility programs" and occasional updates of program modules are available for downloading from the TOUGH2 homepage on the web, at `http://www-esd.lbl.gov/TOUGH2/`.

TMVOC includes a tight and visible "version control" system for meeting stringent demands on reliability and referenceability of code applications. Each program unit, when first called during a TMVOC simulation run, writes a brief (typically one line) message specifying its name, version number, date, and purpose. An example from subroutine MULTI is shown in Fig. 1.1. Version number and/or date are updated when significant modifications are made. This allows reference to user's notes for code changes, and maintains a referenceable record of code changes and applications. All version messages are optionally printed to OUTPUT at the end of a simulation run; for an example see Fig. 10.5.9.

```
      SAVE ICALL
      DATA ICALL/0/
      ICALL=ICALL+1
      IF(ICALL.EQ.1) then
         WRITE(11,899)
c 899 FORMAT(/6X,'MULTI    1.0       9 MAY       1991',6X,
c 899 FORMAT(/6X,'MULTI    1.01      7 MAY       1993',6X,
c 899 FORMAT(/6X,'MULTI    1.01 S   24 June      1994',6X,
...
...
c 899 FORMAT(/6X,'MULTI    1.1       8 October   1999',6X,
c 899 FORMAT(/6X,'MULTI    1.1      15 November  2000',6X,
c 899 FORMAT(/6X,'MULTI    1.1       5 January   2001',6X,
  899 FORMAT(/6X,'MULTI    1.1      10 January   2001',6X,
     X'ASSEMBLE ALL ACCUMULATION AND FLOW TERMS'/
     x47X,'includes capabilities for radiative heat transfer',
     x' and diffusion in all phases'/
     x50X,'with local equilibrium phase partitioning between gas',
     x' and liquid'/
     x47X,'allows block-by-block permeability modification'/
     x47X,'permeability changes from precip. (EWASG) through',
     x' PAR(NLOC2S+3)'/
       x47X,'TMVOC-compatible version'/)
```

Figure 1.1. Example of coding for internal version control.

This report provides a self-contained document for applications of TMVOC. It incorporates much of the material presented in the documentation for TOUGH2, Version 2.0 (Pruess et al., 1999), and includes a brief summary of process models and fluid property descriptions, a reference to code architecture and design, detailed instructions for preparing input data, and a series of sample problems. The mathematical model and complete instructions for preparing input data are provided in appendices.

2. Hardware Requirements and Code Installation

TMVOC was developed on an IBM RS/6000 workstation under a Unix-based operating system. The code has also been tested in a PC environment using a Compaq Deskpro equipped with a Pentium III processor under the Windows NT operating system. Coding complies with the ANSI X3.9-1978 (FORTRAN77) standard. Like other members of the TOUGH/MULKOM family of codes, TMVOC requires 64-bit arithmetic. It is available as a FORTRAN77 program that is intrinsically single precision, and may be used on 64-bit processors, or on 32-bit processors with compiler options for generating double-precision arithmetic. For example, on an IBM RS/6000 workstation with a 32-bit CPU compilation should be made with the option "`-qautodbl=dblpad`" to obtain 64-bit arithmetic; on Sun workstations the same effect is achieved by specifying the "`-r8`" compilation option.

The standard TMVOC FORTRAN77 source code consists of the files `t2fm.f, T2, emvoc.f, t2cg22.f, meshm.f, t2f.f, t2solv.f,` and `ma28.f`. Most of TMVOC uses standard T2V2 (TOUGH2, Version 2.0) program units. TMVOC-specific routines include the fluid property module emvoc.f, and a series of T2V2 routines, bundled into a file t2fm.f, that have been slightly modified to accommodate additional data needs and features of TMVOC. t2cg22.f is an updated version of the "front end" for the preconditioned conjugate gradient solvers, T2 is an INCLUDE file to be used with t2cg22.f, meshm.f performs mesh generation, t2f.f is the main body of T2V2 that performs time stepping and iterative solution of mass and energy balance equations, t2solv.f is a suite of conjugate gradient solvers, and ma28.f is a sparse direct solver. To illustrate the assembly of TMVOC, we list the compilation and linking commands that would be used on an IBM RISC/6000 workstation.

```
f77 -c -qautodbl=dblpad t2fm.f emvoc.f t2cg22.f meshm.f t2f.f t2solv.f ma28.f
f77 -o ztm t2fm.o emvoc.o t2cg22.o meshm.o t2f.o t2solv.o ma28.o
```

The "`-qautodbl=dblpad`" instruction is required to obtain 64-bit arithmetic on a 32-bit processor. Various levels of compilation optimization may be used but are not indicated in the command line given above. Execution of an input file `rblm` (second sample problem, see section 10) would be made with the command

```
ztm <rblm >rblm.out
```

where output is printed to file `rblm.out`.

The t2fm.f and emvoc.f modules include specialized versions of some of the same program units that appear in standard TOUGH2, creating a situation of "duplicate names" during the linking process. On many computers the linker will simply use the first program unit with a given name, and will ignore subsequent program units with the same name, perhaps issuing a warning message in the process. This is the desired outcome. The order of program modules in the linking instruction, above, is significant in that some of the subroutines in t2fm.f are supposed to supersede subroutines with the same name in t2cg22.f and t2f.f; some of the subroutines in emvoc.f should supersede earlier ones in t2f.f. On some computers the presence of duplicate names during linking will create a fatal error. The simplest way of remedying this problem is to change the names of the unwanted program units. For example, t2fm.f includes a modified version of subroutine MULTI; to avoid a conflict the name of MULTI in file t2f.f should be changed to MULTIX prior to compilation.

Memory requirements of TMVOC depend on the problem size, and can be estimated from

$$M = 0.08*(NEL+2*NCON)*NEQ*NEQ \qquad (2.1)$$

where M is RAM in kilobytes, NEL is the number of grid blocks (elements), NCON is the number of connections between them, and NEQ is the number of equations (mass and heat balances) per grid block. Thus, a flow problem with up to 800 grid blocks, 2,400 connections, and 3 equations per grid block can be solved with 4 Megabytes of RAM, while simulation of a problem with 8,000 grid blocks, 24,000 connections, and 4 equations per grid block would require approximately 72 MB of RAM. Eq. (2.1) is approximate in that it does not account for size-independent storage requirements that need to be met even for small problems. The major problem-size dependent arrays can be easily re-dimensioned for different-size problems through the INCLUDE file T2 and through PARAMETER statements in the main program (see section 6.5).

3. Physical Processes and Assumptions

In the TMVOC formulation, the multiphase system is assumed to be composed of water, non-condensible gases (NCGs), and water-soluble volatile organic chemicals (VOCs). The number and nature of NCGs and VOCs can be specified by the user. There are no intrinsic limitations to the number of NCGs or VOCs in the TMVOC formulation; arrays for fluid components are currently dimensioned as 20, accommodating water plus 19 components that may be NCGs or VOCs. NCG arrays are dimensioned as 10. NCGs may be selected by the user from a data bank provided in TMVOC; currently available choices include O_2, N_2, CO_2, CH_4, ethane, ethylene, acetylene, and air (a pseudo-component treated with properties averaged from N_2 and O_2). In most TMVOC applications, just a single NCG, air, will be present. Thermophysical property data for VOCs must be provided by the user. The fluid components may partition (volatilize and/or dissolve) among gas, aqueous, and NAPL phases. Any combination of the three phases may be present, and phases may appear and disappear in the course of a simulation. In addition, VOCs may be adsorbed by the porous medium, and may biodegrade according to a simple half-life model.

Each phase flows in response to pressure and gravitational forces according to a multiphase extension of Darcy's law, which includes effects of relative permeability and capillary pressure between the phases. Transport of the mass components may also occur by molecular diffusion in all phases. Multiphase diffusion is treated in a fully-coupled manner that can cope with diffusion of phase-partitioning components under conditions of variable phase saturations. No Fickian model for hydrodynamic dispersion is implemented at the present time. In heterogeneous media dispersion is often caused by mass exchanges between pore regions with different fluid mobilities (Coats and Smith, 1964; Harvey and Gorelick, 2000), and such effects can be modeled with TMVOC using the method of "multiple interacting continua" (MINC; Pruess and Narasimhan, 1985).

It is assumed that the three phases are in local chemical and thermal equilibrium, and that no chemical reactions are taking place other than (a) interphase mass transfer, (b) adsorption of chemical components to the solid phase, and (c) decay of VOCs by biodegradation. Mechanisms of interphase mass transfer for the organic chemicals include evaporation and boiling, dissolution into the aqueous phase, condensation of organic chemicals from the gas phase into a NAPL, and equilibrium phase partitioning of organic chemicals between the gas, aqueous, and solid phases. Interphase mass transfer of the water component includes the effects of evaporation and boiling of the aqueous phase, condensation of water vapor from the gas phase, and water dissolution into the NAPL phase. The interphase mass transfer of the non-condensible gas components consists of equilibrium phase partitioning between the gas, aqueous, and NAPL phases.

Heat transfer occurs due to conduction and multiphase convection; heat flow associated with diffusive fluxes is neglected. The heat transfer effects of phase transitions between the NAPL, aqueous and gas phases are fully accounted for by considering the transport of both latent and sensible heat. However, heat of dissolution effects for NCG dissolution in NAPL and aqueous phases and for water in the NAPL are neglected, as are heat effects associated with adsorption/desorption of VOCs. The overall porous medium thermal conductivity is calculated as a function of total liquid saturation (water and NAPL).

The saturation pressure, density and internal energy of water are computed, within experimental accuracy, using the International Formulation Committee correlations (IFC, 1967) implemented in the TOUGH2 code. Dynamic viscosity of liquid water and steam is calculated using the correlation proposed by the International Association for the Properties of Steam (Meyer et al., 1977). Thermophysical properties of the NAPL phase such as saturated vapor pressure and viscosity are calculated as functions of temperature and composition, while specific enthalpy and density are computed as function of temperature, composition, and pressure. Vapor pressure lowering effects due to capillary forces are not presently included in the simulator. Gas phase thermophysical properties such as specific enthalpy, viscosity, density, and component molecular diffusivities are considered to be functions of temperature, pressure, and gas phase composition. The solubility of the organic chemical in water may be specified as a function of temperature, and Henry's coefficient for dissolution of organic chemical vapors in the aqueous phase is calculated as a function of temperature. The Henry's coefficients for NCG dissolution in the aqueous phase are calculated as functions of temperature, whereas Henry's coefficients for NCG dissolution in NAPL have for simplicity been assumed to be constant. Water solubility in a generic NAPL is computed as a function of temperature.

The necessary NAPL/organic chemical and transport properties are computed by means of a very general thermodynamic formulation, which uses semi-empirical corresponding states methods in which chemical parameters are calculated as functions of the critical properties of the chemical such as the critical temperature and pressure. Because these data are available for hundreds of organic compounds (Reid et al., 1987), the NAPL/organic chemical equation of state is quite flexible in its application. The gas phase is treated as a mixture of "real" (not ideal) gases.

Porosity may change as a function of fluid pressure and temperature, using simple concepts of pore compressibility and expansivity. No stress calculations are made in TMVOC.

4. Fluid Properties

The fluid description in TMVOC includes arbitrary multiphase mixtures of $\kappa = 1, ..., NK$ mass components, including water ($\kappa = 1$), NCG non-condensible gases ($\kappa = 2, 3, ..., 1+NCG$), and NHC user-selected VOCs ($\kappa = 1+NCG+1, 1+NCG+2, ..., 1+NCG+NHC = NK$), which we often refer to as "hydrocarbons." The NK fluid components may be distributed in any combination of one, two, or three phases, namely, $\beta = 1$: gas, a multi-component mixture of NCGs, water vapor, and hydrocarbon vapors; $\beta = 2$: aqueous, which for convenience is often referred to as "water," and may include dissolved hydrocarbons and NCGs in addition to water substance; and $\beta = 3$: oil or NAPL phase, whose primary constituents are the NHC hydrocarbon components, but which may contain both dissolved water and NCGs.

Depending on thermodynamic conditions and relative abundance of the different components, the fluids may exist in seven different phase combinations, as shown in Fig. 4.1. Arrows denote routes for appearance or disappearance of phases that are checked after each update of thermodynamic conditions during the Newton-Raphson iteration process. We now proceed to a detailed discussion of the model and correlations used for compositions and thermophysical properties of the three phases. For the most part our presentation closely follows Adenekan (1992) and Adenekan et al. (1993).

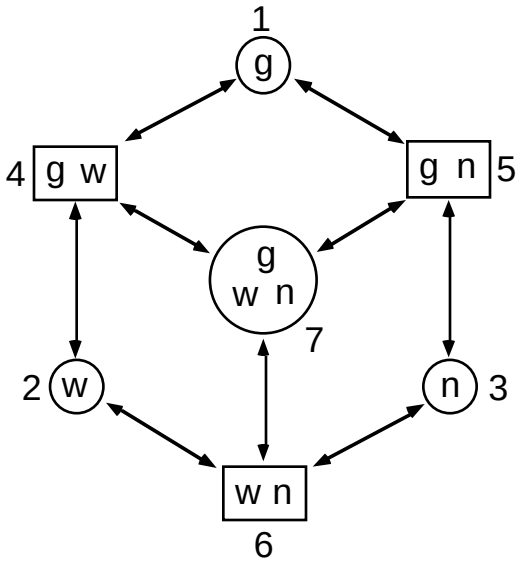


Figure 4.1. Phase compositions and phase changes considered by TMVOC. The phase designations are: g - gas, w - water (aqueous), n - NAPL.

The individual fluid components partition among different phases in such a way that their chemical potentials are the same in all phases (Prausnitz et al., 1986).

$$\mu_g^\kappa = \mu_w^\kappa = \mu_n^\kappa \tag{4.1}$$

It is customary to write the chemical potential for the gas phase as

$$\mu_g^\kappa = \varphi_g^\kappa x_g^\kappa P_g \tag{4.2}$$

where φ_g^κ is the fugacity coefficient of component κ, x_g^κ is its mole fraction, and P_g is the total pressure of the gas phase. For the liquid phases (β = w-water, n-NAPL) we write

$$\mu_\beta^\kappa = \gamma_\beta^\kappa x_\beta^\kappa f_\beta^{\kappa,0} \tag{4.3}$$

where γ_β^κ is the activity coefficient of component κ, x_β^κ is its mole fraction, and $f_\beta^{\kappa,0}$ is the fugacity of component κ in phase β at some fixed condition known as the standard state (Prausnitz et al., 1986).

TMVOC assumes ideal mixtures, with all fugacity and activity coefficients equal to one. Partitioning of components among phases can then be written in terms of mole fraction ratios being equal to equilibrium constants, such as

$$\frac{x_w^\kappa}{x_n^\kappa} = K_{wn}^\kappa; \quad \frac{x_w^\kappa}{x_g^\kappa} = K_{wg}^\kappa; \quad \frac{x_n^\kappa}{x_g^\kappa} = K_{ng}^\kappa \tag{4.4}$$

Equilibrium constants for the condensible fluid components (VOCs, water) can be expressed in terms of solubilities and vapor pressures, see below.

Real gas and liquid hydrocarbon mixtures exhibit ideal behavior at moderate temperatures and pressures (< 15 bar) (McCain, 1990). The approach used by TMVOC is applicable, therefore, for the conditions normally encountered in environmental contamination problems in the unsaturated and saturated zones. It is not applicable when pressure and temperature conditions are far from ambient, as e.g. in conventional hydrocarbon reservoirs, where phase equilibria must be modeled through the use of experimentally determined distribution coefficients or through an equation of state for real gas and liquid hydrocarbon mixtures. The TMVOC approach has another limitation in that it cannot be used for organic chemicals whose critical temperature is lower than the

maximum temperature reached during the simulation. In this case no vapor saturation pressure can be computed for the chemical and thus no equilibrium calculations are possible using the approach followed for a conventional VOC in TMVOC. Methane, in particular, has a critical temperature of - 82.6 °C, and ethane too has a low critical temperature of 32.35 °C. VOCs that are not condensible at prevailing temperature conditions can be treated as NCGs. Properties of the NAPL phase are assumed independent of the concentration of dissolved NCGs.

4.1 Gas Phase

Composition

At ambient conditions, the main constituent of the gas phase will be air. TMVOC can represent air as a single pseudo-component, or as a mixture of N2 and O2. Other non-condensible gases may also be included, see data block NCGAS in Appendix E. In addition, VOC vapors will be present in concentrations that depend upon VOC concentrations in the aqueous phase (or the NAPL phase, if it exists), and upon the VOC vapor pressures which depend strongly on temperature. Water vapor may be present at partial pressures up to saturated values for the given temperature. Vapor pressure lowering from capillary effects is neglected, so that in the presence of an aqueous phase, vapor partial pressure will always be equal to saturated vapor pressure. At elevated temperatures, gas phase composition may be dominated by water and/or VOC vapors. Assuming that gas phase fugacity coefficients and liquid phase activity coefficients are equal to one, we have from Eqs. (4.1) - (4.3)

$$x_g^\kappa P_g = x_\beta^\kappa f_\beta^{\kappa,0} \tag{4.1.1}$$

so that the partial pressures $P_g^\kappa = x_g^\kappa P_g$ of gas phase components are proportional to their mole fractions. When an aqueous phase is present, VOC concentrations in the gas phase are related to dissolved concentrations in the aqueous phase as follows. Applying Eq. (4.1.1) to a three-phase system with a pure VOC component, we obtain

$$P_{vap}^\kappa = x_w^{\kappa,sol} f_w^{\kappa,0} \tag{4.1.2}$$

which expresses the standard-state fugacity of VOC component κ in the aqueous phase in terms of its saturated vapor pressure P_{vap}^κ and aqueous solubility $x_w^{\kappa,sol}$. Introducing this into Eq. (4.1.1) we obtain

$$x_g^\kappa P_g \;=\; x_w^\kappa \left(P_{vap}^\kappa \big/ x_w^{\kappa,sol} \right) \tag{4.1.3}$$

This is a statement of Henry's law, with Henry's coefficient given by $P_{vap}^\kappa \big/ x_w^{\kappa,sol}$. For a single-component NAPL phase in equilibrium with a gas phase, we have $P_{vap}^\kappa = f_n^{\kappa,0}$, so that Eq. (4.1.1) leads to

$$x_g^\kappa P_g \;=\; x_n^\kappa P_{vap}^\kappa \tag{4.1.4}$$

This is a statement of Raoult's law, according to which the vapor pressure of a component κ in a multicomponent liquid is proportional to its mole fraction in the liquid.

Thermophysical properties

PVT properties of the gas phase are usually described with the Soave-Redlich-Kwong (SRK) equation of state (Redlich and Kwong, 1949; Soave, 1972). This is a cubic equation which is commonly used for petroleum reservoir fluids and other nonpolar organic substances. For a pure component the SRK equation may be written in the form

$$Z^3 - Z^2 + \left(A^* - B^* - (B^*)^2 \right) Z - A^* B^* \;=\; 0 \tag{4.1.5}$$

where the largest root Z is the real gas compressibility factor, and $A^* = aP/R^2T^2$ and $B^* = bP/RT$ are parameters that depend on pressure P and absolute temperature T, with R the universal gas constant. The molar density of the gas phase is given by

$$\rho_g \;=\; P/(R\,T\,Z) \tag{4.1.6}$$

Parameters a and b are given by Reid et al. (1987) in terms of critical pressure P_c and critical temperature T_c as

$$a \;=\; \frac{0.42748\,R^2\,T_c^2}{P_c} \left[1 + \left(0.48 + 1.574\,\omega - 0.176\,\omega^2 \right) \left(1 - \left[T/T_c \right]^{1/2} \right) \right]^2 \tag{4.1.7}$$

$$b \;=\; \frac{0.08664\,R\,T_c}{P_c} \tag{4.1.8}$$

Here ω is Pitzer's acentric factor. The multicomponent versions of these parameters are written in terms of parameters a_κ, b_κ and gas phase mole fractions x_g^κ of the individual components κ using the mixing rules recommended by Reid et al. (1987).

$$a_m = \left(\sum_\kappa x_g^\kappa (a_\kappa)^{1/2} \right)^2 \tag{4.1.9}$$

$$b_m = \sum_\kappa x_g^\kappa b_\kappa \tag{4.1.10}$$

In Eqs. (4.1.9) and (4.1.10) all binary interaction parameters have been neglected. Optionally a version of the SRK equation with modified coefficients or the Peng-Robinson (PR) equation (Peng and Robinson, 1976) may be used. The latter is written

$$Z^3 - (1 - B^*)Z^2 + \left(A^* - 2B^* - 3(B^*)^2 \right) Z - \left(A^* B^* - (B^*)^2 - (B^*)^3 \right) = 0 \tag{4.1.11}$$

Gas phase specific enthalpy per mole is calculated relative to a reference temperature T^R as

$$h_g = \left(h(P - P_{H_2O}, T) - h^0(T) + \int_{T^R}^{T} C_p^0 \, dT \right) \sum_{\kappa \neq H_2O} x_g^\kappa + x_g^{H_2O} h_g^{H_2O} \tag{4.1.12}$$

T^R is arbitrary as long as it is used consistently and is here taken to be 0 °C. The integral represents the ideal gas enthalpy at temperature T, and $h(P - P_{H_2O}, T) - h^0(T)$ is the real gas departure enthalpy, excluding water vapor with a partial pressure of P_{H_2O}. Based on the SRK equation the departure enthalpy is

$$h(P - P_{H_2O}, T) - h^0(T) = \left(\frac{a_m}{b_m} - \frac{T}{b_m} \frac{\partial a_m}{\partial T} \right) \ln \left[\frac{Z}{Z + B_m^*} \right] + RT(Z - 1) \tag{4.1.13}$$

where water component (vapor) is excluded from a_m and b_m. The special treatment for water vapor in Eqs. (4.1.12) and (4.1.13) outside of the framework of the SRK equation was adopted because numerical tests showed that the SRK EOS gave a poor approximation to vapor enthalpy. For the PR equation the departure enthalpy becomes

$$h(P - P_{H_2O}, T) - h^0(T) = \frac{\left(\frac{a_m}{b_m} - \frac{T}{b_m}\frac{\partial a_m}{\partial T}\right)}{2.82284} \ln\left[\frac{Z - 0.4142B^*}{Z + 2.4142B_m^*}\right] + RT(Z-1) \quad (4.1.14)$$

The ideal gas heat capacity for a pure gas component κ at constant pressure is estimated using the method of Joback (Reid et al., 1987)

$$C_p^\kappa = a_\kappa + b_\kappa T + c_\kappa T^2 + d_\kappa T^3 \quad (4.1.15)$$

The parameters a_κ, b_κ, c_κ, and d_κ are experimentally determined constants whose values have been tabulated by Reid et al. (1987) for over 500 organic compounds. The molar heat capacity of the multicomponent mixture is obtained as a mole fraction-weighted average of the individual C_p^κ.

Gas phase viscosity μ_g is obtained in terms of pure component viscosities μ_κ as a function of pressure, temperature and composition using the method of Wilke (1950), which is a simplification of the Chapman-Enskog kinetic theory.

$$\mu_g = \sum_{\kappa=1}^{N} \frac{x_g^\kappa \mu_\kappa}{\sum_{\lambda=1}^{N} x_g^\lambda \Phi_{\kappa\lambda}} \quad (4.1.16)$$

The $\Phi_{\kappa\lambda}$ are binary interaction parameters given by

$$\Phi_{\kappa\lambda} = \frac{\left[1 + (\mu_\kappa/\mu_\lambda)^{1/2} (M_\lambda/M_\kappa)^{1/4}\right]^2}{\left[8(1 + M_\kappa/M_\lambda)\right]^{1/2}} \quad (4.1.17)$$

with M_κ the molecular weight of component κ. Viscosities of the individual gas phase components are calculated as follows. Viscosities of non-condensible gases are obtained as functions of temperature in polynomial form after Irvine and Liley (1984)

$$\mu = \sum B_i T^i \quad (4.1.18)$$

VOC viscosities are computed using a corresponding states method (Reid et al., 1987). Viscosity of water and water vapor is obtained from the IAPS formulation (IAPS, 1975).

4.2 Aqueous (Water) Phase

Composition

The dominant constituent of the aqueous phase is water. VOCs may be present in concentrations that depend on temperature-dependent solubilities, and on VOC concentrations in gas or oil phases, if present. The equations for phase partitioning of VOCs in the presence of a gas phase were already given in section 4.1. If no gas phase is present, partitioning between water and NAPL phases is determined from Eqs. (4.1) and (4.3). Setting activity coefficients equal to one, we have

$$x_w^\kappa = x_n^\kappa f_n^{\kappa,0} \big/ f_w^{\kappa,0} \tag{4.2.1}$$

Applying this relation to a single-component NAPL, it is seen that

$$f_n^{\kappa,0} \big/ f_w^{\kappa,0} = x_w^{\kappa,sol} = K_{wn}^\kappa \tag{4.2.2}$$

where $x_w^{\kappa,sol}$ is aqueous phase solubility. NCG dissolution in the aqueous phase is described by Henry's law

$$P_{NCG} = K_H x_w^{NCG} \tag{4.2.3}$$

K_H is Henry's coefficient for NCG dissolution in water. For O_2, N_2, CO_2, CH_4, and air, K_H is computed from a polynomial fit to experimental data as a function of temperature (Battistelli et al., 1997). Constant values appropriate for near-ambient temperatures are used for ethane, ethylene, and acetylene. The user may also optionally choose a constant value $K_H = 10^{10}$ Pa for air, as used in T2VOC (Falta et al., 1995).

Thermophysical properties

Density and specific enthalpy of pure water are given, within experimental accuracy, by the steam table equations issued by the International Formulation Committee (IFC, 1967). Viscosity of pure water is calculated from a formulation due to the International Association for the Properties of Steam (IAPS) given in the ASME steam tables (Meyer et al., 1977).

The solubility of VOCs in the aqueous phase is usually small, typically of the order of a few hundred ppm. It may appear, then, that the presence of such a small amount of VOC in the aqueous phase would have negligible impact on the aqueous phase density, and that sufficient accuracy

would be attained by taking the aqueous phase density equal to that of pure water, regardless of how much VOC may be dissolved. A closer examination of the issue reveals, however, that neglecting the impact of dissolved VOC on the aqueous phase density may result in unacceptably large spurious pressure excursions. Consider the dissolution of TCE with a density of 1462 kg/m^3 at ambient conditions in water with an ambient density of 998 kg/m ^{3}. If TCE were permitted to dissolve in the aqueous phase without any density change of the latter, then the dissolution process would be accompanied by an increase in total fluid volume. If fluid volume were held constant an increase in fluid pressure would result which can be estimated as follows. At the solubility limit a mass fraction of approximately 10^{-3} of TCE is present in the aqueous phase. Dissolving this amount of NAPL in an aqueous phase of constant density, at constant pressure, would cause a relative increase in the volume of the water-NAPL two-phase mixture of $\Delta V/V \approx 0.068$ %. If fluid volume were held constant, a pressure increase of $\Delta P = (\Delta V/V)/c_w \approx 1.36 \times 10^6$ Pa would result. The reason for this surprisingly large increase is in the small compressibility of liquid water, $c_w \approx 5 \times 10^{-10}$ Pa^{-1} at ambient conditions. These estimates were confirmed by means of numerical dissolution experiments.

Accordingly, a better density model was implemented for the aqueous phase that avoids these problems (Falta et al., 1995). The basic assumption we make is that, when NAPL dissolves in water, both total fluid mass and total fluid volume are conserved. Denoting water and NAPL phase volumes by V_w and V_n, respectively, the volume of the aqueous phase after NAPL dissolution is given by

$$V_{aq} = V_w + V_n \tag{4.2.4}$$

Similarly, the total number of moles present in the aqueous phase is

$$m_{aq} = m^w + m^n \tag{4.2.5}$$

Dividing Eq. (4.2.4) by (4.2.5) and inserting the mole fractions $x^w = m^w/m_{aq}$ of water and $x^n = m^n/m_{aq}$ of dissolved VOC, we obtain for the molar density of the aqueous phase $\rho_{aq} = m_{aq}/V_{aq}$.

$$\frac{1}{\rho_{aq}} = \frac{V_{aq}}{m_{aq}} = \frac{x^w}{\rho_w} + \frac{x^n}{\rho_n} \tag{4.2.6}$$

In the TMVOC implementation x^w is replaced by $(1 - x^n)$. Effects on aqueous phase enthalpy and viscosity from dissolution of VOCs and NCGs are neglected.

4.3 Oil (NAPL) Phase

Composition

This phase consists primarily of condensed VOCs, with usually small admixtures of dissolved water and NCGs.

The solubility of water in VOCs is generally small. Dependence on composition of the NAPL phase is neglected, and temperature dependence is given by a regression formula on water solubility data for generic NAPLs (Hoot et al., 1957).

$$x_n^w = 0.281226 - 4.23610\,\nu + 1.75244\,\nu^2 \qquad (4.3.1)$$

where $\nu = \log10(1.8T_C + 32)$, with T_C the temperature in degrees Celsius. NCG dissolution in the NAPL phase is described with Henry's law, cf. Eq. (4.2.3); the same values of Henry's coefficient as for water is used for anorganic NCGs.

Thermophysical properties

For calculating density the oil phase is assumed to be an ideal mixture of the VOC components; effects of the small solubilities of water and NCG on NAPL density are neglected. Thus molar volume v_n of the NAPL phase is given as a sum of the partial molar volumes v_κ of the VOC components.

$$v_n = \sum_{\kappa \neq \text{water,NCG}} x_n^\kappa v_\kappa \qquad (4.3.2)$$

Molar volumes of individual components are calculated as a function of temperature from the Rackett equation (Reid et al., 1987)

$$v_\kappa = v_\kappa^R \left(0.29056 - 0.08775\omega_\kappa\right)^{\varphi_\kappa} \qquad (4.3.3)$$

where v_κ^R is molar volume of component κ at reference temperature T^R, ω_κ is the acentric factor, and the exponent is given by

$$\varphi_\kappa = (1 - T/T_{c\kappa})^{2/7} - (1 - T^R/T_{c\kappa})^{2/7} \qquad (4.3.4)$$

with $T_{c\kappa}$ the critical temperature of component κ. A simple pressure dependence of NAPL density is accounted for according to

$$\rho_n = \frac{\exp\left(c_n\left[P - P_{ref}\right]\right)}{\nu_n} \tag{4.3.5}$$

where $c_n = 2\text{x}10^{-9}$ Pa^{-1} is the isothermal compressibility of a generic NAPL, and $P_{ref} = 1.01325\text{x}10^5$ Pa is a reference pressure.

The specific molar enthalpy of a pure liquid VOC component κ is calculated by means of the following decomposition

$$\begin{aligned} h_\kappa^L(T,P) = \; & h_\kappa^{L,R} + (h_\kappa - h_\kappa^L) + (h_\kappa^L - h_\kappa^V) + (h_\kappa^V - h_0) \\ & + (h_0 - h_0^R) + (h_0^R - h_\kappa^{V,R}) + (h_\kappa^{V,R} - h_\kappa^{L,R}) \end{aligned} \tag{4.3.6}$$

Here $h_\kappa^{L,R}$ is liquid enthalpy at a reference temperature T^R and corresponding saturated vapor pressure $P_{sat}(T^R)$, h_κ^L and h_κ^V are, respectively, the enthalpy of saturated liquid and vapor at conditions of $(T, P_{sat}(T))$, h_0 is the ideal gas enthalpy at temperature T, h_0^R is the ideal gas enthalpy at temperature T^R, and $h_\kappa^{V,R}$ is the enthalpy of saturated vapor at reference conditions of $(T^R, P_{sat}(T^R))$. The individual components of NAPL phase enthalpy are evaluated as follows. $h_\kappa - h_\kappa^L$ represents the effect of pressure on enthalpy which for a liquid phase is small and is neglected in TMVOC. $h_\kappa^L - h_\kappa^V$ and $h_\kappa^{V,R} - h_\kappa^{L,R}$ are enthalpies of vaporization and are calculated as follows. For a pure liquid the enthalpy of vaporization at the normal boiling point is computed by the Chen method (Reid et al., 1987)

$$\Delta h_{vb} = R\,T_c\,T_{br}\,\frac{3.978\,T_{br} - 3.958 + 1.555\ln P_c}{1.07 - T_{br}} \tag{4.3.7}$$

where $T_{br} = T_b/T_c$, with T_c the critical temperature. Enthalpy of vaporization at the temperature of interest is then obtained from the Watson correlation (Reid et al., 1987)

$$\Delta h_v = \Delta h_{vb}\left(\frac{1 - T_r}{1 - T_{br}}\right)^{0.375} \tag{4.3.8}$$

Here, $T_r = T/T_c$ is the reduced temperature. $h_0 - h_0^R$ is the difference between ideal gas enthalpies at temperatures T and T^R and is calculated as $\int_{T^R}^{T} C_p^0\,dT$. The terms $h_\kappa^V - h_0$ and $h_0^R - h_\kappa^{V,R}$ are

gas phase departure enthalpies which are calculated in analogy to Eq. (4.1.12). The specific molar enthalpy of the NAPL phase is then obtained from those of the pure components as

$$h_n = \sum_\kappa x_n^\kappa \left(h_\kappa^L - h_\kappa^{L,R} \right) \tag{4.3.9}$$

where the summation is over all VOC components. Heat of mixing effects are neglected in Eq. (4.3.9), as are effects of dissolved NCG or water.

Saturated vapor pressures of pure VOC components are calculated from the Wagner equation (Reid et al., 1987)

$$P_{vap} = P_c \exp\left\{ \left[a(1-T_r) + b(1-T_r)^{1.5} + c(1-T_r)^3 + d(1-T_r)^6 \right] / T_r \right\} \tag{4.3.10}$$

Values of the constants a, b, c, d for several VOCs are given in Appendix A of Reid et al. (1987). When these parameters are not available, vapor pressure will be calculated from the less accurate Antoine correlation

$$\ln P_{vap} = A - \frac{B}{T + C} \tag{4.3.11}$$

where A, B, and C are empirical constants that have been tabulated by Reid et al. (1987) for over 500 compounds.

Viscosity of a pure VOC component is calculated as a function of temperature from an equation due to Yaws et al. (1976)

$$\ln \mu = A' + \frac{B'}{T} + C' T + D' T^2 \tag{4.3.12}$$

A simpler correlation with C' = D' = 0 was used by van Velzen et al. (1972). Values of the constants can be found in chapter 9 of Reid et al. (1987). The mixture viscosity of the NAPL phase is obtained in terms of the pure component viscosities as

$$\mu_n = \prod_\kappa \mu_\kappa^{x_n^\kappa} \tag{4.3.13}$$

This is one of many approximations proposed in the literature for correlating mixture viscosities. Pressure dependence of VOC viscosity is neglected.

4.4 Adsorption of VOCs

Adsorption of VOCs on the solid grains is modeled as reversible instantaneous linear sorption. The mass of VOC component κ adsorbed per unit reservoir volume is written as (Eq. A.3)

$$M^{\kappa}_{ads} = (1-\phi)\rho_R \rho_w x^{\kappa}_w K_d \qquad (4.4.1)$$

where ϕ is porosity, ρ_R is the density of the rock grains, ρ_w is the density of the aqueous phase, x^{κ}_w is the mole fraction of VOC component κ in the aqueous phase, and K_d is the aqueous phase distribution coefficient (de Marsily, 1986, p. 256). The use of (4.4.1) assumes that some liquid water is present in the system, and that the medium is preferentially wetted by the aqueous phase. In very dry systems, the use of Eq. (4.4.1) to describe vapor adsorption may lead to some error. It has been found that the degree of adsorption of organic chemicals depends largely on the amount of organic carbon present in the soil. Accordingly, K_d is often written as

$$K_d = K_{oc} f_{oc} \qquad (4.4.2)$$

where K_{oc} is the organic carbon partition coefficient, and f_{oc} is the organic carbon fraction in the medium (Karickhoff et al., 1979; Schwarzenbach and Westall, 1981).

4.5 Biodegradation

TMVOC includes a simple approximate representation of biodegradation of VOCs. It is assumed that VOCs dissolved in the aqueous phase may decay according to the standard exponential decay law

$$d M^{\kappa}_w = -\lambda_{\kappa} M^{\kappa}_w \, dt \qquad (4.5.1),$$

where $M^{\kappa}_w = \phi S_w \rho_w x^{\kappa}_w$ is the mass of VOC component κ in the aqueous phase per unit reservoir volume, and the rate constant λ_{κ} is related to the half-life $T_{\kappa,1/2}$ as $\lambda_{\kappa} = \ln 2/T_{\kappa,1/2}$. This decay process is represented by incorporating a sink term ($q^{\kappa} < 0$) into Eq. (A.1).

$$q^{\kappa} = -\lambda_{\kappa} M^{\kappa}_w \qquad (4.5.2)$$

5. Implementation in TMVOC

5.1 Scope and Methodology

TMVOC solves mass and energy balance equations that describe fluid and heat flow in general multiphase, multicomponent systems (Appendix A). For numerical simulation the continuous space and time variables must be discretized (see Appendix B). In all members of the TOUGH2 family of codes, space discretization is made directly from the integral form of the basic conservation equations, without converting them into partial differential equations. This "integral finite difference" method (IFDM; Edwards, 1972; Narasimhan and Witherspoon, 1976) avoids any reference to a global system of coordinates, and thus offers the advantage of being applicable to regular or irregular discretizations in one, two, and three dimensions. The IFDM also makes it possible, by means of simple preprocessing of geometric data, to implement double- and multiple-porosity methods for fractured media (see Appendix C; Pruess and Narasimhan, 1982, 1985; Pruess, 1983a). No particular price needs to be paid for this flexibility; indeed, for systems of regular grid blocks referred to a global coordinate system the IFDM is completely equivalent to conventional finite differences. Time is discretized fully implicitly as a first-order backward finite difference. This together with 100 % upstream weighting of flux terms at interfaces is necessary to avoid impractical time step limitations in flow problems involving phase (dis-)appearances, and to achieve unconditional stability (Peaceman, 1977).

The discretization results in a set of strongly coupled nonlinear algebraic equations (Appendix B), with the time-dependent primary thermodynamic variables of all grid blocks as unknowns. These equations are cast in residual form, i.e., {residual} $\equiv$ {left-hand side} - {right-hand side} = 0, and are solved simultaneously, using Newton-Raphson iteration. Time steps can be automatically adjusted (increased or reduced) during a simulation run, depending on the convergence rate of the iteration process. Automatic time step adjustment is essential for an efficient solution of multiphase flow problems, where intrinsic time scales for significant changes in the flow system may vary by many orders of magnitude during a simulation run. Different methods are available to solve the linear equations arising at each iteration step, including preconditioned conjugate gradient solvers, as well as sparse direct matrix methods (see section 7.6). While direct methods are more predictable and less problem-dependent in their performance, it is only through the application of iterative conjugate gradient methods that solutions for large grid systems (10,000 blocks or more) and three-dimensional problems can be accomplished (Moridis and Pruess, 1998).

The accuracy of TMVOC has been tested against analytical solutions and by comparison with numerical results obtained from T2VOC as well as other TOUGH2 modules. TOUGH2

simulations have been compared with many different analytical and numerical solutions, with results from laboratory experiments, and with field observations (see e.g., Moridis and Pruess, 1992; Pruess et al., 1996). However, users are cautioned that there is no finite process by which all program bugs that may be present can be identified and corrected. Many different options can be selected in different program units. It is not practically possible to exhaustively cross-check the mutual compatibility and proper performance of all options. Fixing a bug may cause unanticipated problems elsewhere. Continuing vigilance and application testing are needed.

5.2 Program Structure and Execution

The governing equations for multiphase fluid and heat flow (see Appendix A) have the same mathematical form, regardless of the nature and number of fluid phases and components present. TMVOC uses the modular TOUGH2 architecture (see Fig. 5.2.1), in which the main flow and transport module interfaces with the fluid property module by means of two large arrays.

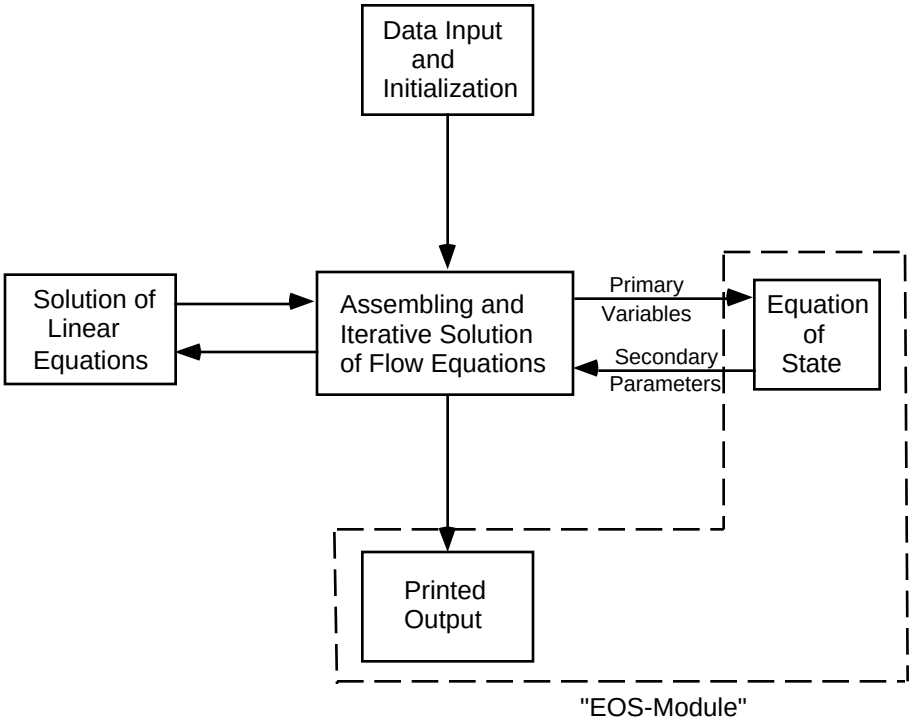


Figure 5.2.1. Modular architecture of TMVOC.

These hold, respectively, the primary thermodynamic variables for all grid blocks, and all other (secondary) thermophysical parameters needed to assemble the governing flow and transport equations (see section 6.2). These arrays are one-dimensional and hold data for all grid blocks of the computational mesh in sequential fashion. The solution of a flow problem essentially consists

of a complete set of thermodynamic variables as a function of time. In TMVOC, all arrays holding spatially distributed information take the form of labeled COMMON blocks, one per array. This provides flexibility and convenience for adjusting array dimensions to different-size problems.

The subroutines contained in the TMVOC package can be grouped according to their functions as summarized in Table 1. The initialization of a simulation run is accomplished by the subroutines INPUT and RFILE in a flexible manner.

Table 1. TMVOC program structure

subroutine(s)	function
TOUGH2 (main program)	executive routine; define problem-size dependent arrays, generate internal documentation
INPUT, RFILE (and satellite routines, including MESHMaker)	problem initialization
CYCIT	executive routine for time stepping
EOS (and satellites)	thermophysical properties and phase diagnostics
MULTI (and satellites)	assembly of mass and energy balance equations
QU (and satellites)	sink and source terms
LINEQ (and satellites)	solution of linear equations, provisional updating of thermodynamic variables
CONVER	conclusion of converged time steps, updating of thermodynamic variables and iteration counters
WRIFI, OUT, BALLA	output of results

Most of the necessary data are supplied from disk files, which can be either directly provided by the user, or can be generated internally from data provided in the INPUT file. The initialization stage also can generate a variety of computational grids, or meshes. The iteration sequence for time stepping is controlled by CYCIT. On the first time step, all thermophysical properties are initialized in subroutine EOS (with a large number of satellite routines for PVT calculations), and time step counter KCYC, iteration counter ITER, and convergence flag KON are defined. The iteration counter is incremented, and the accumulation and flow terms for all equations are assembled in subroutine MULTI. If sinks or sources are present MULTI calls subroutine QU, which in turn can call a series of satellite routines to perform functions such as calculating phase compositions of produced fluids, and interpolating time-dependent data from tables. MULTI then computes the

residuals for all of the mass and energy balance equations, identifies the element index (NER) and equation index (KER) for the largest residual, and checks for convergence. If convergence is achieved the flag KON is set to 2, and CONVER is called to update the primary variables. Otherwise control shifts to LINEQ, which functions as executive routine for the linear equation solution, and can call a variety of user-selectable linear equation solvers. Informative messages during the linear equation solution process are written onto a disk file called LINEQ. Printed output subject to different user controls can be generated with subroutines OUT and BALLA. Depending on the value of the convergence flag KON, the program will proceed to the next iteration (KON = 1), or to the next time step (KON = 2). If anything goes wrong - failure in computing thermophysical parameters, failure in solving the linear equations, failure to converge within a given maximum number of iterations - the time step will be repeated with a reduced time increment Δt.

Execution will continue until one of several termination criteria is reached, such as a user-specified total number of time steps, or a specified simulation time. In some cases a simulation may proceed with convergence achieved on the first iteration (ITER = 1). This can occur when time steps are chosen so small, or conditions are so close to steady state, that the convergence tolerances are satisfied without requiring any updating of thermodynamic variables. TMVOC has coding to recognize such a condition. If convergence on ITER = 1 occurs for 10 consecutive time steps, this will be taken to indicate attainment of steady state, the current conditions will be written out, and execution will terminate.

Another termination criterion is monitored when automatic time step control is in effect. In this case execution will be stopped when convergence failure is encountered following two time steps for which convergence on ITER = 1 was achieved. The rationale for this is as follows. As conditions approach steady state, the rates of change in thermodynamic variables become small, and time steps will grow to very large values when automatic time step control is in effect. The off-diagonal elements in the Jacobian matrix are proportional to time step size, and may become so large that convergence of the linear equation system may no longer be achieved because of numerical roundoff. Thus we may have a situation where for a somewhat reduced time step convergence is achieved without requiring a linear equation solution (ITER = 1), while no convergence at all can be obtained when a linear equation solution is required. The aforementioned stopping criterion was designed to prevent such “no progress” calculations to go on and on for a potentially large number of user-specified time steps.

A general overview of TMVOC input data is presented in section 7; Appendices E and F provide a full reference to TMVOC input formats.

6. TMVOC Array Structure

6.1 Primary Thermodynamic Variables

TMVOC implements the assumption that locally all phases are in thermodynamic equilibrium. Let us now consider the number of primary thermodynamic variables that are needed to completely specify the thermodynamic state of a flow system consisting of NK components, which are distributed according to local thermodynamic equilibrium among NPH phases. From Gibbs' phase rule it follows that the number of thermodynamic degrees of freedom in such a system is

$$f = NK + 2 - NPH \tag{6.1.1}$$

In addition there are (NPH – 1) saturation degrees of freedom, because the NPH phase saturations (or phase volume fractions) S_β are constrained by the relationship

$$\sum_{\beta=1}^{NPH} S_\beta = 1 \tag{6.1.2}$$

The total number of primary thermodynamic variables (degrees of freedom) is therefore

$$\begin{aligned} NK1 &= f + NPH - 1 \\ &= NK + 1 \end{aligned} \tag{6.1.3}$$

which is equal to the total number of balance equations per grid block, namely, NK mass balance and one energy balance equation. The thermodynamic state of a discretized flow system consisting of NEL volume elements, or grid blocks, is then completely specified by a set of NEL*NK1 primary thermodynamic variables, to which correspond an equal number of mass and energy balance equations. For transient flow systems, these primary variables are time-dependent, and they represent the unknowns to be calculated in each time step. While the number of balance equations per grid block is usually NEQ = NK+1, TMVOC can also operate in an isothermal mode where no energy balance is solved, so that then NEQ = NK.

An important consideration in the modeling of fluid and heat flow processes with phase change is the choice of the primary variables that define the thermodynamic state of the system. When a phase appears or disappears, the set of appropriate thermodynamic variables may change. For example, in single-component flows involving just water, natural thermodynamic variables for

describing single-phase conditions (subcooled liquid or superheated steam) are temperature T and pressure P. However, in two-phase conditions pressure and temperature are not independent, but are related by the vapor-pressure relationship $P = P_{sat}(T)$. Two-phase conditions may be described using either (T, S) (S = saturation) or (P, S) as primary variables, requiring a "switching" of primary variables during phase change. Experience has proven variable-switching to be a very robust method for treating multiphase systems, and this is the approach used in TMVOC. In addition to temperature, pressure, and saturation, mole fractions x_β^κ of mass components $\kappa = 1, ..., NK$ in phases β = g, w, n are used as primary variables. Mass components are labeled in the following order: water comes first, followed by the NCG (≥ 1) non-condensible gases, and the NHC VOCs come last, see Table 2.

Table 2. Labeling of mass components.

index	component
1	water
2	NCG #1
...	...
1+NCG	NCG #NCG
2+NCG	VOC #1
...	...
NK = NHC+1+NCG	VOC # NHC

Fluid components are identified in TMVOC by their index numbers as shown in Table 2. This numbering is used in the assignment of source specifications. For example, injection of mass component #n is accomplished by specifying a generation type 'COMn', see below. The specification of primary thermodynamic variables as shown in Table 3 is different from the ordering of mass components. The first primary variable is always pressure. In single-phase conditions (Index = 1, 2, 3) this is the pressure of the single fluid phase present. When a gas phase is present (Index = 1, 4, 5, 7) the pressure is gas phase pressure. For two-phase water-NAPL conditions (Index = 6), P is the pressure of the NAPL phase. Pressures of other fluid phases may differ by a capillary pressure that is a function of saturation (Appendix H). The primary variables following pressure refer to VOC mole fractions in different phases, except that in three-phase conditions mole fraction of the first VOC is not a primary variable; instead gas saturation is used as primary variable and occupies the slot that for other phase combinations holds the mole fraction of

the first VOC. Following the VOC mole fractions are mole fractions of the non-condensible gases. However, when more than one phase is present, mole fraction of the last NCG is not a primary variable and a phase saturation appears in that slot instead. The last primary variable is always temperature, which must be specified even when an isothermal calculation is desired.

Table 3. Primary thermodynamic variables used by TMVOC.

Phase Conditions	Phase Index	Primary Variables ⇐ ⇐ ⇐ ⇐ VOCs ⇐ | ⇒ NCGs ⇒ ⇒ ⇒ ⇒							
			VOC #1	···	VOC #NHC	NCG #1	···	NCG #NCG	
		1	2	···	NHC + 1	NHC + 2	···	NK	NK+1
gas only	1	P	x_g^{2+NCG}	...	x_g^{NK}	x_g^2	...	x_g^{1+NCG}	T
water only	2	P	x_w^{2+NCG}	...	x_w^{NK}	x_w^2	...	x_w^{1+NCG}	T
NAPL only	3	P	x_n^{2+NCG}	...	x_n^{NK}	x_n^2	...	x_n^{1+NCG}	T
gas and water	4	P	x_g^{2+NCG}	...	x_g^{NK}	x_g^2	...	S_w	T
gas and NAPL	5	P	x_g^{2+NCG}	...	x_g^{NK}	x_g^2	...	S_n	T
water and NAPL	6	P	x_n^{2+NCG}	...	x_n^{NK}	x_n^2	...	S_w	T
three phase	7	P	S_g	...	x_g^{NK}	x_g^2	...	S_w	T

6.2 Change of Phase Composition

Here we elaborate on the techniques used to handle the appearance and disappearance of fluid phases in the course of a simulation. Our presentation closely follows Adenekan (1992) and Adenekan et al. (1993).

After each step of the Newton-Raphson iteration process the primary thermodynamic variables are updated, and fluid phase compositions are checked, separately for each grid block, for consistency against the new values of the primary variables. If it is found that a fluid phase either appears or disappears, the phase index and the primary thermodynamic variables are changed according to Table 3. Disappearance of a phase is easier to recognize than appearance. For example, consider a grid block that was in two-phase gas-water conditions prior to the latest Newtonian iteration. Then water saturation S_w is among its primary variables, and disappearance of the aqueous phase would be easily recognized when the latest updated $S_w < 0$. Similarly, the gas phase would disappear if $S_w > 1$.

Checking for the possible appearance of a phase involves a thermodynamic criterion. In the case of two-phase gas-water conditions, the possibility of a NAPL phase appearing is tested by evaluating the mole fractions that the different VOC components would have in a NAPL phase. Phase partitioning calculations as discussed in section 4 are performed to derive the x_n^κ corresponding to latest iterated values of the primary x_g^κ variables. In order for a NAPL-phase to exist the sum of these mole fractions must exceed 1, i.e.

$$\sum_\kappa x_n^\kappa \quad > \quad 1 \tag{6.2.1}$$

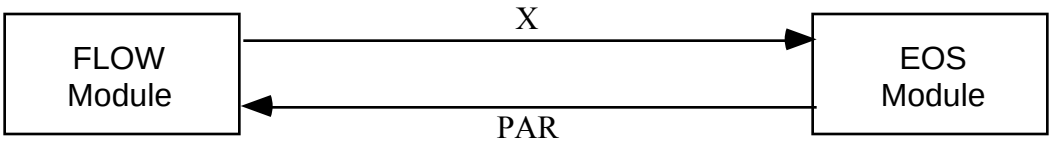
is the criterion that must be satisfied if a NAPL phase is to evolve. Practically it is found that simulator performance is more robust when a "finite window" is used for phase appearance. That is to say, a transition to three-phase g-w-n conditions is made only when $\sum_\kappa x_n^\kappa$ exceeds 1 by a finite amount, which we take to be of order 10^{-3}.

After the phase composition of a grid block changes, primary thermodynamic variables may have to be re-initialized to be consistent with the new phase composition. If a new phase appears, its saturation is initialized as a small $S = 10^{-6}$. Mole fractions may change dramatically during phase appearance; for example, when a NAPL phase evolves from VOCs that are either dissolved in the aqueous phase or volatilized in the gas phase, mole fractions of different VOCs in the water or gas phase may be quite differently affected, due to different solubility and vapor pressure constraints.

The progress of the simulation with new phase composition can depend sensitively on the initialization of VOC mole fractions. Ideally the new phase compositions should be obtained by equilibrating a multicomponent mixture of known overall composition among the fluid phases present. This requires what in the chemical engineering literature is known as a "flash calculation." TMVOC uses this approach when a NAPL phase evolves from either single-phase gas or two-phase gas-water conditions. For other phase transitions a simpler approach is used, in which newly appearing phases are initialized with a small saturation (10^{-6}) so that their impact on the composition of the other phases is small.

6.3 Thermophysical Property Arrays

In TMVOC all of the NEL*NK1 primary variables are stored sequentially in a one-dimensional array X; first the NK1 variables for grid block # 1, then the NK1 variables for grid block # 2, and so on (see Fig. 6.3.1). The starting location for primary variables for grid block N is NLOC+1, where NLOC = (N-1)*NK1.



Volume Element	Primary Variables
# 1	X(1) • • • X(NK1)
# 2	X(NK1+1) • • • X(2*NK1)
	• • • • •
# N	X(NLOC+1) • • • X(NLOC+NK1)
	• • • • •
# NEL	• • • X(NEL*NK1)

⇒

Volume Element	SECONDARY PARAMETERS		gas phase	aqueous phase
# 1	phase saturation	S	PAR(1)	PAR(NBK+1)
	relative permeability	k_r	PAR(2)	•
	viscosity	μ	PAR(3)	•
	density	ρ	PAR(4)	•
	specific enthalpy	h	PAR(5)	•
	capillary pressure	P_c	PAR(6)	•
	diffusion factor 1(§)	a	PAR(7)	•
	diffusion factor 2(&)	b	PAR(8)	•
	mole fractions			
	component 1	X^1	PAR(NB+1)	•
	•	•	•	•
	component NK	X^{NK}	PAR(NB+NK)	PAR(2*NBK)
	temperature	T	PAR(NSEC-1)	
	(miscellaneous)		PAR(NSEC)	
	(second set of secondary parameters: X(1) incremented)			
			PAR(NSEC+1)	
			•	
			•	
			PAR(2*NSEC)	
			•	
			•	
			•	
			PAR((NEQ+1)*NSEC)	
# 2 • • • # NEL	• • • • •			

(§) $a = \phi \tau_0 \tau_\beta \rho_\beta$ (&) $b = d_\beta^\kappa(T,P) \big/ d_\beta^\kappa(T_0,P_0)$

Figure 6.3.1. Structure of thermophysical property arrays in TMVOC.

The thermophysical properties ("secondary parameters") needed to assemble the mass- and energy-balance equations for all volume elements are stored sequentially in a large array "PAR" (see Fig. 6.3.1). These parameters are calculated in the EOS module for the latest updated primary variables during the iteration process. The first group of NB (= 6 or 8) secondary parameters includes 6 parameters needed for the accumulation and advective flow terms (Eqs. A.2 through A.6). If parameter NB is set equal to 8, these are followed by two parameters for the dependence of diffusion coefficients on primary variables (see Appendix D). Starting in location NB+1, there are NK component mole fractions, so that the total number of secondary parameters per fluid phase is NBK = NB + NK. Mole fractions of the NK mass components are assigned to locations NB+1, NB+2, ..., NB+NK of the PAR array in the order shown in Table 2.

In the PAR-array, the NBK gas phase parameters come first, followed by NBK parameters for the aqueous phase and then NBK parameters for the NAPL phase. Because of space limitations, Fig. 6.3.1 for the PAR array structure shows only the first two fluid phases. The NPH*NBK = 3*NBK phase-specific parameters are followed by temperature T and an additional array member that is not used by TMVOC. The total number of secondary parameters is NSEC = NPH*NBK + 2.

There are two additional arrays DX and DELX with structure identical to X. While X holds primary variables corresponding to the last successful (converged) time step, DX holds the increments calculated during the Newton-Raphson iteration process. Thus the latest updated primary variables are X + DX. Thermophysical properties are needed not only for calculating the residuals of the mass- and energy-balance equations (B.5), but also for calculating their derivatives in the Jacobian matrix $\mathbf{J} = -\partial R_n / \partial x_i$ (see Eqs. B.6 and B.7; x_i denotes the collection of all primary independent thermodynamic variables). In order to avoid any restrictions in the manner that thermophysical parameters could be functionally dependent on primary variables, these derivatives are obtained by numerical differentiation. In order to calculate derivatives, the PAR-array must provide secondary parameters not only at the "state point" (latest X + DX), but also for NEQ additional sets of primary variables in which one of the primary variables at a time is incremented by a small amount. Therefore, the total number of secondary parameters per grid block is (NEQ + 1)*NSEC. Secondary parameters for grid block #N start after location # NLOC2 = (N – 1)*(NEQ +1)*NSEC of the PAR array. The small increments used for numerical differentiation are typically of order 10^{-8} * X, and are stored in an array DELX. The structure of the coupled linear equations solved at iteration step (p+1) is shown in Fig. 6.3.2. The mass balance equations are numbered according to the labeling of mass components, see Table 2. At the conclusion of a converged time step, the primary variables X are updated, X → X + DX.

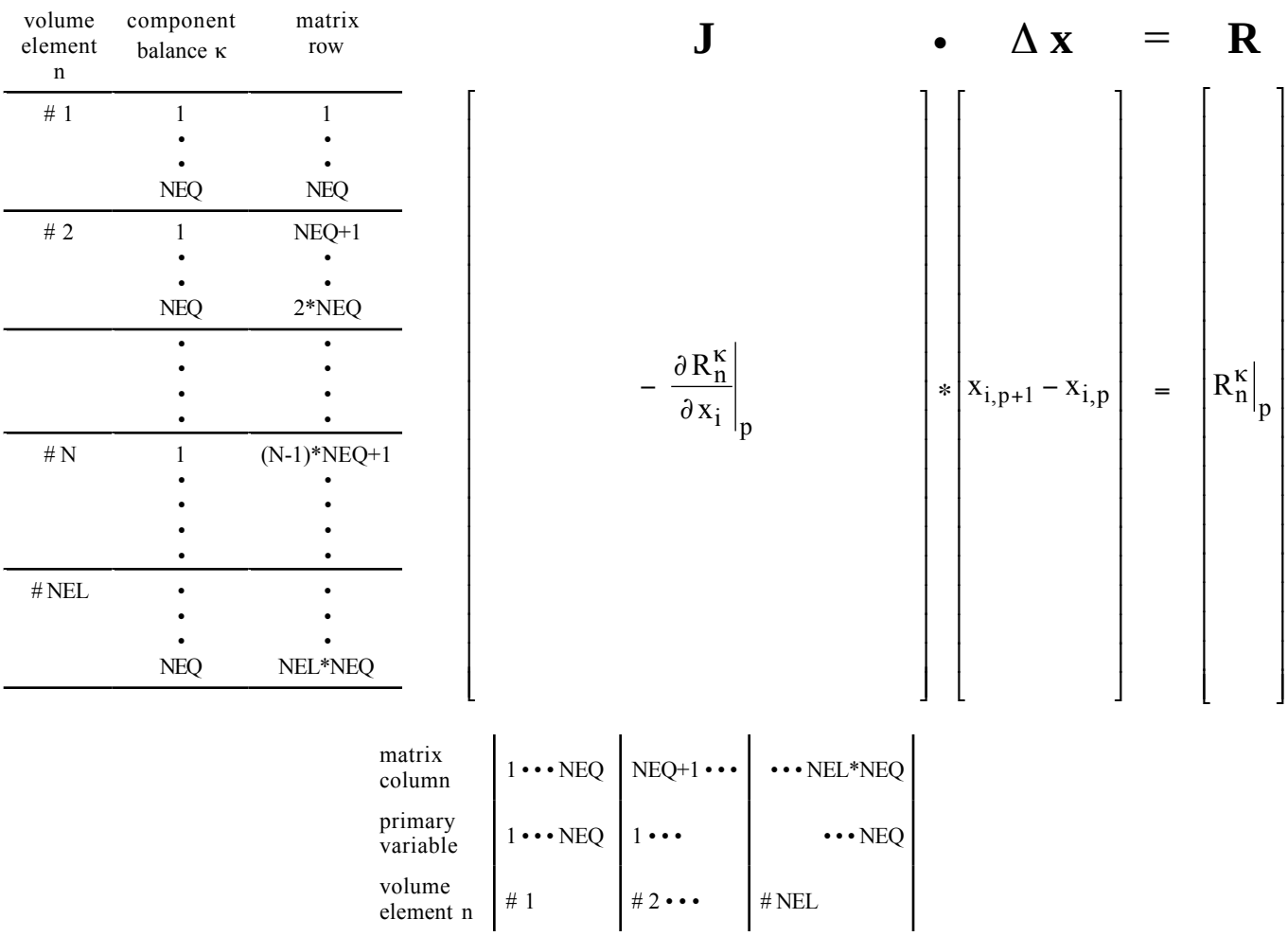


Figure 6.3.2. Linear equation structure.

It was stated above that the number of mass- and energy-balance equations per grid block is the same as the number NK1 of primary thermodynamic variables. In many applications, however, heat effects and temperature changes may be small, so that it would be sufficient to consider just the mass balance equations. The simplest way of forcing temperature changes to zero would be to assign the solid matrix an overwhelmingly large heat capacity, so that finite rates of heat exchange will cause negligible temperature change. This approach is perfectly acceptable and useable with TMVOC, but it has the disadvantage that the full number of balance equations must be solved, even though the energy balance reduces to the trivial statement $\partial T/\partial t = 0$. TMVOC offers a more elegant way of running problems without temperature changes, at a considerable savings of computing time. By convention we always take the first NK equations per grid block to represent mass balances, while the energy balance equation comes last as # NK1. TMVOC uses a parameter NEQ,

distinct from NK, to number the balance equations per grid block, and normally we would have NEQ = NK + 1. However, the user can choose to assign NEQ = NK in the input file; then no energy equations are set up or solved and the number of coupled equations per grid block is reduced by one. For the smaller set of NK equations we only solve for the first NK primary variables, so that temperature remains unchanged (see Table 3).

6.4 Linear Equation Setup

The data provided by the PAR-array are used in the flow module of TMVOC to assemble the linear equations (B.7) that are solved at each step of the Newton-Raphson iteration procedure. These equations are arranged and numbered sequentially, as shown in Fig. 6.3.2, with the first NK equations per grid block representing component mass balances, while the last equation (# NK1) represents the energy balance. The row indices of the Jacobian matrix correspond to the component balance equations in the order given in Table 2, followed by the energy balance, while the column indices correspond to the sequence of primary variables in array X. If the option NEQ = NK is chosen, only NK mass balance equations will be set up per grid block. In this case only the first NK primary variables per grid block will contribute matrix columns, while variable # NK1, which must be temperature, remains passive and is not engaged or altered in the linear equation handling. However, all thermophysical parameters will be calculated at the temperature values specified in variable # NK1.

Note that the accumulation terms of the balance equations depend only on primary variables for one grid block (see Eqs. A.2 - A.4), so that they will generate non-zero derivative terms only in an NEQ*NEQ submatrix that is located on the diagonal of the Jacobian J. The flow terms, being dependent on primary variables of two grid blocks, will generate two non-zero NEQ*NEQ submatrices of derivatives, which are located in the off-diagonal matrix locations corresponding to the two grid blocks.

In TMVOC all Jacobian matrix elements as well as the entries in the vector R of residuals are calculated in subroutine MULTI. The calculation first assigns all matrix elements arising from the accumulation terms, of which there are NEQ*NEQ. These are stored sequentially in a one-dimensional array CO; matrix elements for grid block N begin after location (N – 1)*NEQ*NEQ in CO. The corresponding row and column indices are stored separately in arrays IRN and ICN, respectively. Calculation of the derivatives demands that each accumulation term is calculated NEQ + 1 times; once for the state point (X + DX), and NEQ times for each of the NEQ primary variables incremented (X + DX + DELX). Additional contributions to diagonal terms in the Jacobian **J** may arise from sink and source terms if present; these are assigned in subroutine QU

called from MULTI. Subsequently all flux terms are evaluated. These depend in general on the 2*NEQ primary variables of the two connected grid blocks, so that a total of 2*NEQ + 1 flux terms need to be evaluated for calculation of the state point as well as of all derivative terms. The total number of potentially non-zero elements in the Jacobian matrix is

$$NZ = NEL * NEQ**2 + 2 * NCON * NEQ**2 \qquad (6.4.1)$$

After all matrix elements and members of the right-hand side vector of residuals have been assembled, the linear equations (B.7) are solved by one of several user-selectable algorithms, including sparse direct methods and a variety of preconditioned conjugate gradient algorithms (see section 8.6). The resulting increments in the primary variables are added to the array DX, and the process of linear equation setup and solution is repeated for the primary variables X + DX. This process continues until the residuals are reduced below a preset convergence tolerance (Eq. B.8). If convergence is not achieved within a specified maximum number of iterations (usually 8) the time step is repeated with reduced time increment.

6.5 Dimensioning of Major Arrays

The major problem-size dependent arrays reside in labeled COMMON blocks, one array per block. They are dimensioned by means of PARAMETER statements in an INCLUDE file called T2 and in the main (TOUGH2) program. An informational statement on permissible problem size (number of grid blocks, etc.) is provided in the printed output of a TMVOC run. When problem specifications exceed array dimensions, the execution stops with a diagnostic printout. The user must then increase PARAMETER assignments accordingly. All arrays are given a dimension of 1 in the subroutines, and for re-dimensioning it is only necessary to revise the PARAMETER assignments in the INCLUDE file and in the main program; no other changes are needed. Some compilers will generate warnings or error messages when COMMON blocks are dimensioned differently in different program units. This can be avoided by compiling the main program separately from the subprograms. Subsequent linking of the object modules will properly communicate COMMON block addresses between main program and subprograms. A list of major arrays used in TMVOC and their dimensions is given in Table 4 below.

Table 4. Summary of major common blocks

Reference to	COMMON blocks	Length
Elements	E1 - E7, VINWES, AHTRAN XYZ1, XYZ2, XYZ3, VBC	NEL (= number of elements)
Primary variables	P1 - P7	NEL*NK1
Connections (interfaces)	C1 - C12 COMPO, PORVEL, FLOVP1, FLOVP2 DISP DARVELM	NCON (= number of connections) NCON*NPH NCON*NPH*NK NCON*NPH*(2*NEQ+1)
Sinks and sources	G1, G2, G3, G3A G4 through G25, and G27 through G31 G26	MGTAB (= total number of tabular generation data) NOGN (= number of sinks and sources NOGN*NPH
Secondary parameters	SECPAR	NEL*(NEQ+1)*NSEC
Linear equations†	L1, L2, L3 L4 L5, L8 L6 L7 CGARA6	NZ NEL*NEQ 5*NEL*NEQ 8*NEL*NEQ 5*NEL*NEQ+NZ+32 38*NEL*NEQ+1000

† array dimensioning is made according to the needs of the conjugate gradient solvers; when the direct solvers MA28 or LUBAND are used, only a smaller-size problem can be accommodated; restriction with MA28 is:

{number of elements} + 2 * {number of connections} < {NEL + 2* NCON}/4

7. Preparation of Input Data

The data needed to characterize a flow system include hydrogeologic parameters and constitutive relations of the permeable medium (absolute and relative permeability, porosity, capillary pressure, etc.), thermophysical properties of the fluids (partly provided internally), initial and boundary conditions of the flow system, and sinks and sources. In addition, TMVOC requires specification of space-discretized geometry, and various program options, computational parameters, and time-stepping information. Here we summarize the basic conventions adopted for TMVOC input data. A detailed explanation of TMVOC input data is given in Appendix E; input formats for internal grid generation through the MESHMaker module are explained in Appendix F.

7.1 TMVOC Input Data

Input can be provided to TMVOC in a flexible manner by means of one or several ASCII data files, with up to 80 characters per record. All TMVOC input is in fixed format and most of it is in standard metric (SI) units, such as meters, seconds, kilograms, °C, and the corresponding derived units, such as Newtons, Joules, and Pascal = N/m^2 for pressure. VOC and NCG concentrations are provided as mole fractions, see Table 2, and different customary units are used for the chemical properties of VOCs.

In the standard TMVOC input file, data are organized in blocks which are defined by five-character keywords typed in columns 1-5; see Table 5 and Fig. 7.1.1. The first record must be a problem title of up to 80 characters. The last record usually is ENDCY; alternatively, ENDFI may be used if no flow simulation is to be carried out (useful for mesh generation). Data records beyond ENDCY (or ENDFI) will be ignored. Some data blocks, such as those specifying reservoir domains (ROCKS), volume elements (ELEME), connections (CONNE), initial conditions (INCON, INDOM), and sinks/sources (GENER), have a variable number of records, while others have a fixed number of records. The end of variable-length data blocks is indicated by a blank record. Most data blocks between the first and last one can be provided in arbitrary order, but block MULTI must precede any data on initial conditions (blocks PARAM, INDOM, and INCON), and block ELEME, if present, must precede block CONNE. The blocks ELEME and CONNE must either be both provided through the INPUT file, or must both be absent, in which case alternative means for specifying geometry data will be employed (see section 7.2, below). The block GENER can be omitted if there are no sinks and sources in the problem. If block START is present, consisting of one data record with START typed in columns 1-5, the block INCON can be incomplete, with elements in arbitrary order, or can be absent altogether. Elements for which no initial conditions are specified in INCON will then be assigned domain-specific initial conditions

Table 5. TMVOC input data blocks[§]

Keyword	Function
TITLE (first record)	one data record (single line) with a title for the simulation problem
MESHM	optional; parameters for internal grid generation through MESHMaker
ROCKS	hydrogeologic parameters for various reservoir domains
CHEMP	specifies thermophysical property data for the VOCs
NCGAS	specifies number and type of non-condensible gases
SELEC	optional; specifies real gas EOS to be used and selects K_H for air
MULTI	optional; specifies number of fluid components and balance equations per grid block; useful to invoke an isothermal run, read T2VOC style initial conditions, or make a restart for a new run in which additional hydrocarbons have been added
START	optional; one data record for more flexible initialization
PARAM	computational parameters; time stepping and convergence parameters; program options
DIFFU	diffusivities of mass components
FOFT	optional; specifies grid blocks for which time series data are desired
COFT	optional; specifies connections for which time series data are desired
GOFT	optional; specifies sinks/sources for which time series data are desired
RPCAP	optional; parameters for relative permeability and capillary pressure functions
TIMES	optional; specification of times for generating printout
*ELEME	list of grid blocks (volume elements)
*CONNE	list of flow connections between grid blocks
*GENER	optional; list of mass or heat sinks and sources
INDOM	optional; list of initial conditions for specific reservoir domains
*INCON	optional; list of initial conditions for specific grid blocks
NOVER (optional)	optional; if present, suppresses printout of version numbers and dates of the program units executed in a TMVOC run
ENDFI	alternative to "ENDCY" for closing a TMVOC input file; will cause flow simulation to be skipped; useful if only mesh generation is desired
ENDCY (last record)	one record to close the TMVOC input file and initiate the simulation

§ Blocks labeled with a star * can be provided as separate disk files, in which case they would be omitted from the INPUT file.

from block INDOM, if present, or will be assigned default initial conditions given in block PARAM, along with default porosities given in block ROCKS. If START is not present, INCON must contain information for all elements, in exactly the same order as they are listed in block ELEME.

Between data blocks an arbitrary number of records with arbitrary data may be present in the input file that do not begin with any of the TMVOC keywords. This is useful for inserting comments about problem specifications directly into the input file. TMVOC will gather all these comments and will print the first 50 such records in the output file.

Much of the data handling in TMVOC is accomplished by means of disk files, which are written in a format of 80 characters per record, so that they can be edited and modified with any text editor. Table 6 summarizes the disk files other than (default) INPUT and OUTPUT used in TMVOC; examples are given for sample problem 1 in section 10.1. The initialization of the arrays for geometry, generation, and initial condition data is always made from the disk files MESH (or MINC), GENER, and INCON. A user can either provide these files at execution time, or they can be written from TMVOC input data during the initialization phase of a run. If no data blocks GENER and INCON are provided in the input file, and if no disk files GENER and INCON are present, defaults will take effect (no generation; domain-specific initial conditions from block INDOM, or defaults from block PARAM). If a user intends to use these defaults, (s)he has to make sure that at execution time no disk files INCON or GENER are present from a previous run (or perhaps from a different problem). A safe way to use default GENER and INCON is to specify "dummy" data blocks in the input file, consisting of one record with GENER or INCON, followed by a blank record. (Include a one-record data block START in this case.)

The format of data blocks ELEME, CONNE, GENER, and INCON is basically the same when these data are provided as disk files as when they are given as part of the input file. However, specification of these data through the input file rather than as disk files offers some added conveniences, which are useful when a new simulation problem is initiated. For example, a sequence of identical items (volume elements, connections, sinks or sources) can be specified through a single data record. Also, indices used internally for cross-referencing elements, connections, and sources will be generated internally by TMVOC rather than having them provided by the user. MESH, GENER, and INCON disk files written by TMVOC can be merged into an input file without changes, keeping the cross-referencing information.

TMVOC INPUT FORMATS

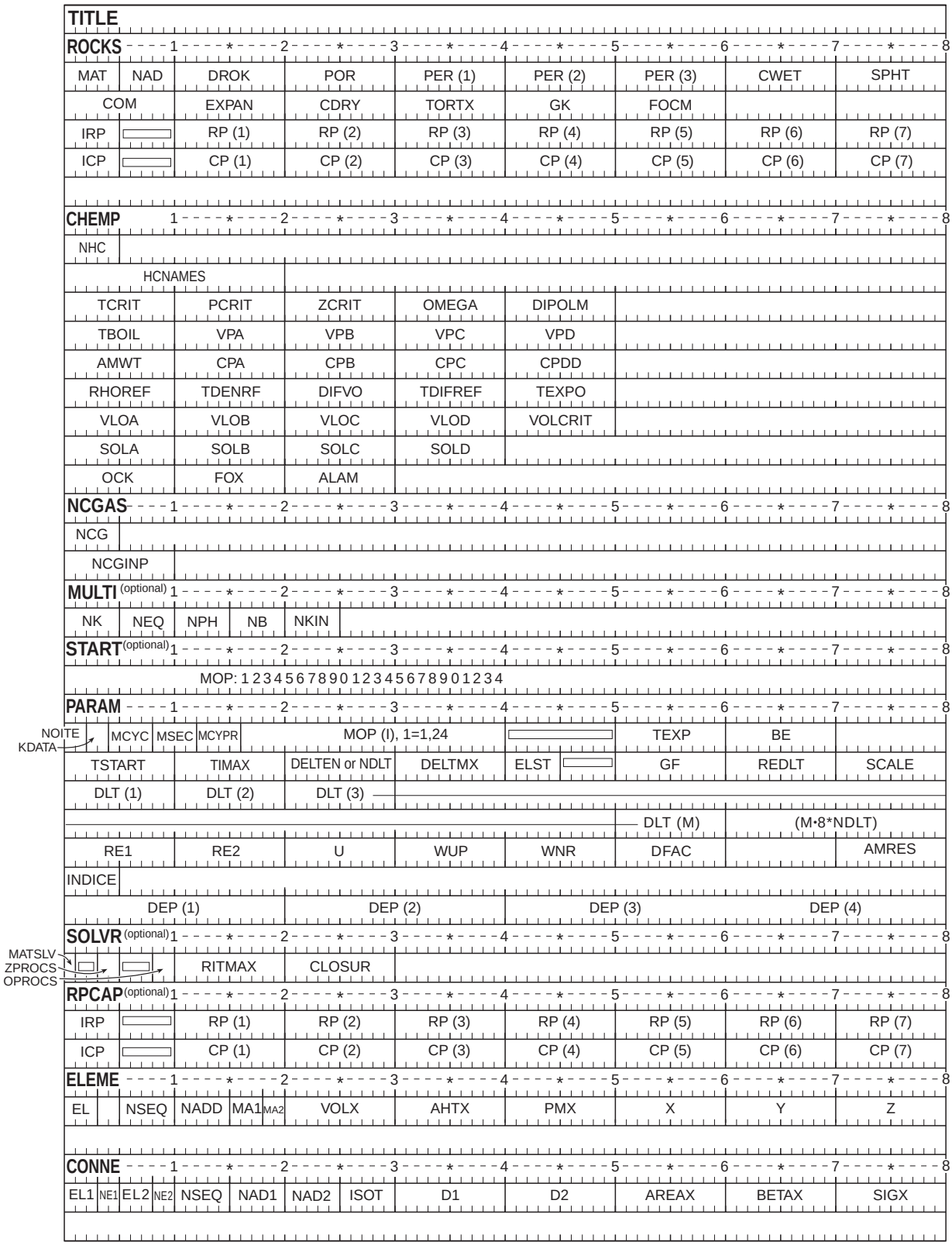


Figure 7.1.1. TMVOC input formats (continued on next page).

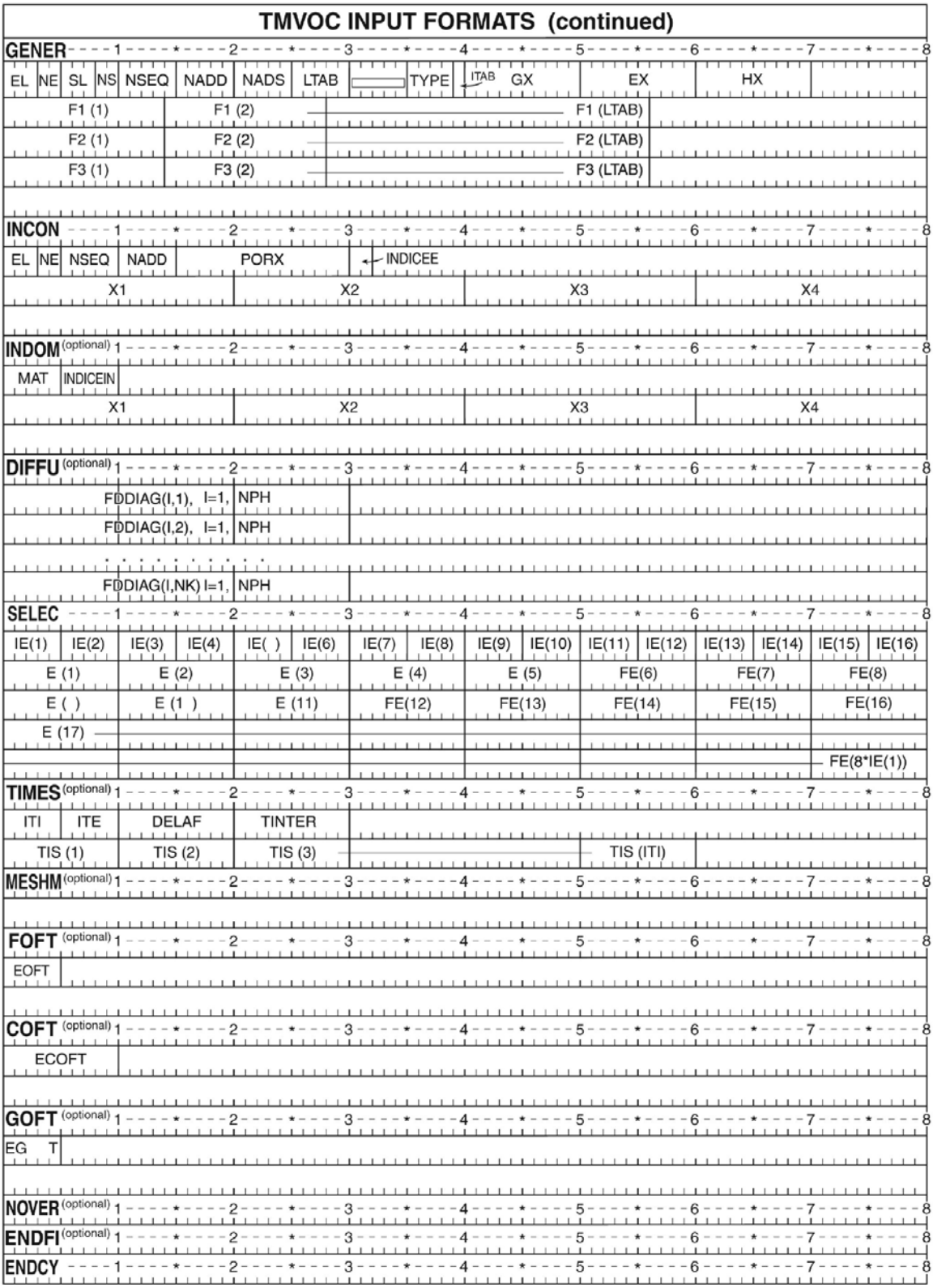


Figure 7.1.1. TMVOC input formats (continued).

Table 6. TMVOC disk files

File	Use
MESH (unit 4)	written in subroutine INPUT from ELEME and CONNE data, or in module MESHMAKER from mesh specification data; read in RFILE to initialize all geometry data arrays used to define the discretized flow problem
GENER (unit 3)	written in subroutine INPUT from GENER data; read in RFILE to define nature, strength, and time-dependence of sinks and sources
INCON (unit 1)	written in subroutine INPUT from INCON data; read in RFILE to provide a complete specification of thermodynamic conditions
SAVE (unit 7)	written in subroutine WRIFI to record thermodynamic conditions at the end of a TMVOC simulation run; compatible with formats of file or data block INCON for initializing a continuation run
MINC (unit 10)	written in module MESHMAKER with MESH-compatible specifications, to provide all geometry data for a fractured-porous medium mesh (double porosity, dual permeability, etc.); read (optionally) in subroutine RFILE to initialize geometry data for a fractured-porous system
LINEQ (unit 15)	written during linear equation solution, to provide informative messages on linear equation solution
TABLE (unit 8)	written in CYCIT to record coefficients of semi-analytical heat exchange at the end of a TMVOC simulation run read (optionally) in subroutine QLOSS to initialize heat exchange coefficients in a continuation run
FOFT (unit 12)	written in FGTAB to provide time series data for elements for plotting
COFT (unit 14)	written in FGTAB to provide time series data for connections for plotting
GOFT (unit 13)	written in FGTAB to provide time series data for sinks/sources for plotting
VERS (unit 11)	written in all TMVOC program units with informational message on version number, date, and function; read in main program and printed to default OUTPUT at the conclusion of a TMVOC simulation run; printing of version information is suppressed when keyword NOVER is present in INPUT file

7.2 Geometry Data

General Concepts

Handling of flow geometry data in TMVOC is based on the "integral finite difference" method (Edwards, 1972; Narasimhan and Witherspoon, 1976). Flow geometry is defined by means of a list of volume elements ("grid blocks"), and a list of flow connections between them (Appendix B). This formulation can handle regular and irregular flow geometries in one, two, and three dimensions. Single- and multiple-porosity systems (porous and fractured media) can be specified, and higher order methods, such as seven- and nine-point differencing, can be implemented by means of appropriate specification of geometric data (Pruess and Bodvarsson, 1983).

In TMVOC, volume elements are identified by names that consist of a string of five characters, '`12345`'. These are arbitrary, except that the last two characters (#4 and 5) must be numbers; an example of a valid element name is "`ELE10`". Flow connections are specified as ordered pairs of elements, such as "(`ELE10`, `ELEll`)". A variety of options and facilities are available for entering and processing geometric data (see Fig. 7.2.1). Element volumes and domain identification can be provided by means of a data block ELEME in the INPUT file, while a data block CONNE can be used to supply connection data, including interface area, nodal distances from the interface, and orientation of the nodal line relative to the vertical. These data are internally written to a disk file MESH, which in turn initializes the geometry data arrays used during the flow simulation. It is also possible to omit the ELEME and CONNE data blocks from the INPUT file, and provide geometry data directly on a disk file MESH.

Meshmaker

TMVOC offers an additional way for defining flow system geometry by means of a special program module MESHMaker. This can perform a number of mesh generation and processing operations and is invoked with the keyword MESHMaker in the INPUT file. The MESHMaker module itself has a modular structure; present sub-modules include RZ2D for generating two-dimensional radially symmetric (R-Z) meshes, and XYZ for one-, two-, and three-dimensional rectilinear (Cartesian) grids. Multiple-porosity processing for simulation of flow in naturally fractured reservoirs can be invoked by means of a keyword MINC, which stands for "multiple interacting continua" (see Appendix C). The MINC-process operates on the data of the primary (porous medium) mesh as provided on disk file MESH, and generates a "secondary" mesh containing fracture and matrix elements with identical data formats on file MINC. (The file MESH used in this process can be either directly supplied by the user, or it can have been internally

generated either from data in INPUT blocks ELEME and CONNE, or from RZ2D or XYZ mesh-making.)

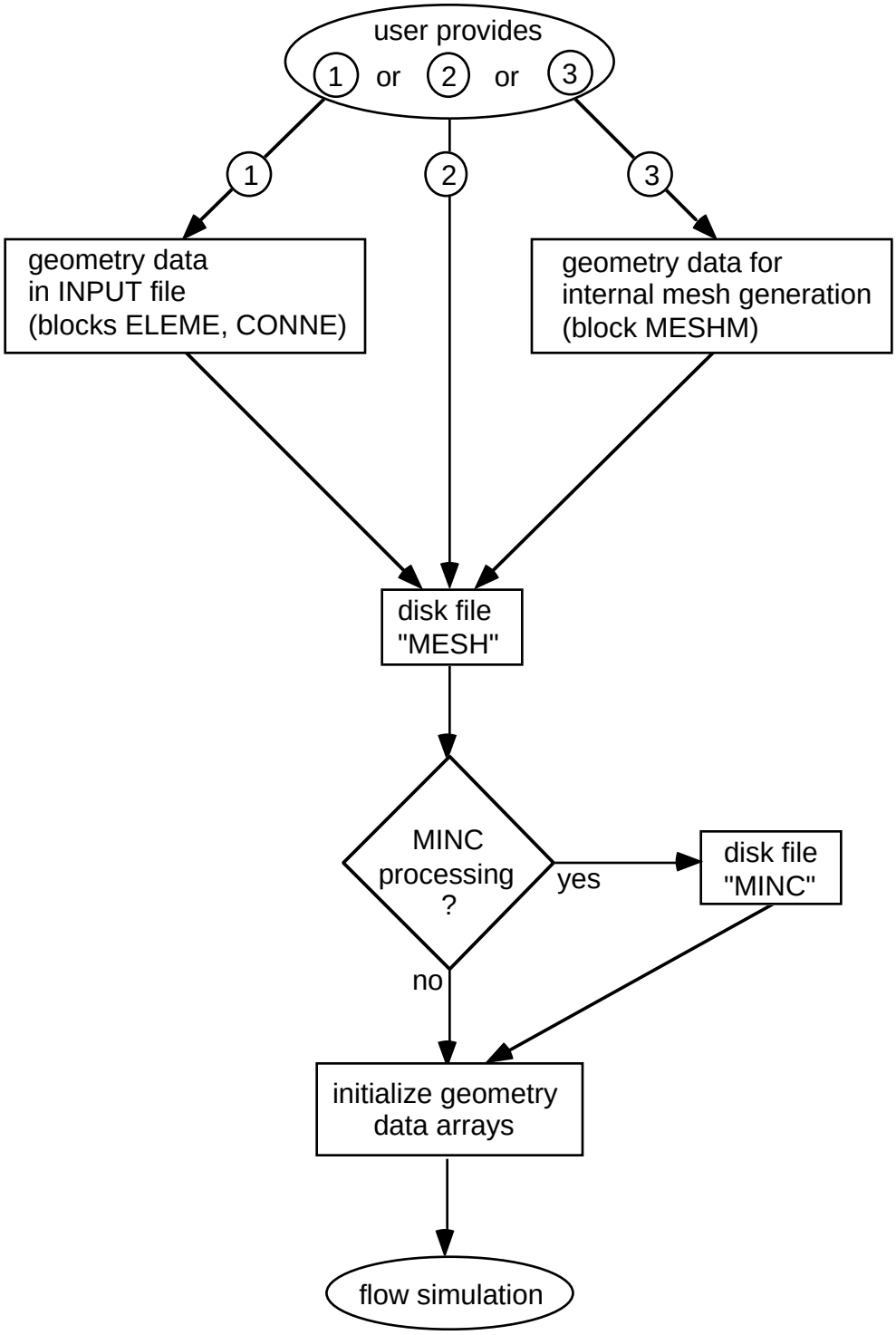


Figure 7.2.1 User options for supplying geometry data.

The MINC process of sub-partitioning porous medium grid blocks into fracture and matrix continua will only operate on active grid blocks, while inactive grid blocks are left unchanged as single porous medium blocks. By convention, elements encountered in data block ELEME (or file MESH) are taken to be "active" until the first element entry with a zero or negative volume is encountered. The first element with volume less than or equal to zero, and all subsequent elements, are taken to be "inactive." In order to exclude selected reservoir domains from the MINC process, the user needs to preprocess or edit the ELEME data block before MINC partitioning is made, and assemble all grid blocks that are to remain single porous media at the end, then place a "dummy" block of zero volume in front of them. The concept of inactive blocks is also used in a second, unrelated manner to maintain time-independent Dirichlet boundary conditions (see section 8.2).

As a convenience for users desiring graphical display of data, the internal mesh generation process will also write nodal point coordinates on file MESH. These data are written in 3E10.4 format into columns 51-80 of each grid block entry in data block ELEME. No internal use whatsoever is made of nodal point coordinates in TMVOC.

Specific naming conventions have been adopted in the internal mesh generation process. For RZ2D, the last two characters directly number the radial grid blocks, from 1 through 99. Character #3 is blank for the first 99 radial blocks, and then runs through the sequence 1, 2, ..., 9, A, B, ..., Z for a maximum total of 3599 radial blocks. The second character counts up to 35 grid layers as 1, 2, ..., 9, A, B, ..., Z. The first character is 'A' for the first 35 layers, and is incremented to B, C, ..., Z, 1, 2, ..., 9 for subsequent groups of 35 layers.

For rectilinear meshes generated by XYZ, characters 4 and 5 together number the grid blocks in the X-direction, while character #3 = 1, 2, ..., 9, A, B, ..., Z numbers Y direction grid blocks, and character #2, running through the same sequence as #3, numbers grid blocks in the Z-direction. Overflows in any of these (more than 99 X-blocks, more than 35 Y- or Z-blocks) advance character #l through the sequence A, B, C, ..., Z. Both RZ2D and XYZ assign all grid blocks to domain #l (first entry in block ROCKS); a user desiring changes in domain assignments must do so by hand, either through editing of the MESH file with a text editor, or by means of preprocessing with an appropriate utility program, or by appropriate source code changes in subroutines WRZ2D and GXYZ. TMVOC runs that involve RZ2D or XYZ mesh generation will produce a special printout, showing element names arranged in their actual geometric pattern. An example is given in section 10.

The naming conventions for the MINC process are somewhat different from those originally adopted in the GMINC program (Pruess, 1983b), and are as follows. For a primary grid block with name '12345,' the corresponding fracture subelement in the secondary mesh is named ' 2345' (character #1 replaced with a blank for easy recognition). The successive matrix continua are labeled by running character #1 through 2, ..., 9, A, B, ..., Z. The domain assignment is incremented by 1 for the fracture grid blocks, and by 2 for the matrix grid blocks. Thus, domain assignments in data block ROCKS should be provided in the following order: the first entry is the single (effective) porous medium, then follows the effective fracture continuum, and then the rock matrix. An example is given in sample problem 4 (*rfp*), see p. 99 of TOUGH2 User's Guide, Version 2.0 (Pruess et al., 1999).

Users should beware that the MINC process may lead to ambiguous element names when the inactive element device is used to keep a portion of the primary mesh as unprocessed porous medium.

Mesh generation and/or MINC processing can be performed as part of a simulation run. Alternatively, by closing the input file with the keyword ENDFI (instead of ENDCY), it is possible to skip the flow simulation and only execute the MESHMaker module to generate a MESH or MINC file. These files can then be used, with additional user-modifications by hand if desired, in subsequent flow simulations. MESHMaker input formats are described in Appendix F, and examples of practical applications are given in the sample problems. Execution of MESHMaker produces printed output which is self-explanatory.

8. User Features

8.1 Initial Conditions and Restarting

Flow systems are initialized by assigning a complete set of primary thermodynamic variables to all grid blocks into which the flow domain is discretized. Various options are available in a hierarchical system, as follows. During the initialization of a TMVOC run, all grid blocks are first assigned to default thermodynamic conditions specified in data block PARAM. The defaults can be overwritten for selected reservoir domains by assigning domain-specific conditions in data block INDOM. These in turn may be superseded by thermodynamic conditions assigned to individual grid blocks in data block INCON. A disk file INCON written to the same specifications as data block INCON may also be used. In TMVOC, the primary variables used depend on the fluid phase composition. During phase change primary variables will be automatically switched from one set to another. In multiphase flow systems, therefore, different grid blocks will in general have different sets of primary variables, and must be initialized accordingly. A TMVOC run may optionally be initialized from T2VOC-style thermodynamic conditions. This is done by appropriate assignment of parameter NKIN in data block MULTI, see Appendix E. For consistency, TMVOC should then be run with a single non-condensible gas (NCG=1), specified as air.

For many applications, special initial conditions are needed, such as gravity-capillary equilibrium, or steady state corresponding to certain mass and heat flows. These can be realized by performing a series of TMVOC runs, in which thermodynamic conditions obtained in one run, and written to disk file SAVE, are used as initial conditions in a subsequent continuation run. For example, a first simulation run may be made to obtain hydrostatic pressure conditions. These may subsequently be used as boundary conditions in a second run segment to simulate the introduction of organic chemicals into the flow system. This could be followed by a third run segment to simulate a remediation process, such as air extraction, groundwater pumping, or steam injection, etc. Restarting of a TMVOC run is accomplished by providing file SAVE generated in a previous run as file INCON for initialization. Usually additional (often minor) adjustments will be made for a restart. For example, different specifications for the number of time steps and desired printout times may be made. Some editing of the MESH file may be needed to make certain grid blocks inactive, so that previously calculated pressures can serve as boundary conditions (see below). In a continuation run, simulation time and time step counters may be continuously incremented, or they may be reset to zero. The latter option will be used when simulating contaminant behavior following preparation of a steady “natural” initial state, which may correspond to a very large simulation time.

As far as the internal workings of the code is concerned, there is no difference between a fresh start of a simulation and a restart. The only feature that makes a simulation a continuation run is that the INCON-data were generated by a previous TMVOC run, rather than having them explicitly provided by the user. File SAVE always ends with a data record with '+++' in the first three columns, followed by one record with restart information (time step and iteration counters, simulation time). To reset all counters to zero, users should simply replace the '+++' with a blank record when using SAVE as file INCON for another TMVOC run.

8.2 Boundary Conditions and "Inactive" Elements

Boundary conditions can be of two basic types. Dirichlet conditions prescribe thermodynamic conditions, such as pressure, temperature, etc. on the boundary, while Neumann conditions prescribe fluxes of mass or heat crossing boundary surfaces. A special case of Neumann boundary conditions is "no flux," which in the integral finite difference framework is handled with simplicity itself, namely, by not specifying any flow connections across the boundary. More general flux conditions are prescribed by introducing sinks or sources of appropriate strength into the elements adjacent to the boundary.

Dirichlet conditions can be implemented by assigning very large volumes (e.g., $V = 10^{50}$ m^3) to grid blocks adjacent to the boundary, so that their thermodynamic conditions do not change at all from fluid or heat exchange with finite-size blocks in the flow domain. In addition, a small value (such as $D = 10^{-9}$ m) should be specified for the nodal distance of such blocks, so that boundary conditions are in fact maintained in close proximity to the surface where they are desired, and not at some distance from it. It is possible to specify a nodal distance that is outright zero; however, this throws certain switches in subroutine MULTI for assignment of interface mobilities that are intended for modeling of fracture-matrix interaction. Therefore, assigning D = 0 should be used with caution.

Time-dependent Neumann conditions can be specified by making sink and source rates time dependent. Time-dependent Dirichlet conditions can also be implemented; these are realized by placing appropriate sinks or sources in the boundary blocks (Moridis and Pruess, 1992). As an example, consider a laboratory experiment reported by Kruger and Ramey (1974) that involved flashing (vaporizing) flow from a sandstone core, with a time-dependent gas pressure boundary condition

$$P_b = P_0 + P_1 t + P_2 t^2 \qquad (8.2.1)$$

maintained at the outflow end. According to the ideal gas law, the pressure behavior of Eq. (8.2.1) can be associated with a time-dependent gas inventory of mass M_b in a volume V as follows.

$$M_b = P_b \left(mV/RT \right) \tag{8.2.2}$$

where m is the molar weight of the gas, R the universal gas constant, and T absolute temperature. The required time dependence of M_b can be realized by means of a sink/source rate

$$Q_b = dM_b / dt = \left(mV/RT \right) dP_b / dt = \left(mV/RT \right)\left(P_1 + 2 P_2 t \right) \tag{8.2.3}$$

Therefore, the desired boundary condition can be implemented by means of a grid block with volume V that is initialized in single-phase gas (e.g., air) conditions, with pressure P_0, and with a time-dependent sink/source term given by Eq. (8.2.3) that would be specified through tabular generation data. In order for the pressure conditions in this block to be negligibly affected by heat and mass exchange with the flow domain, the volume V should be made very large, e.g., $V = 10^{50}$ m^3, just as for time-independent Dirichlet boundary conditions. The time dependent generation rates from Eq. (8.2.3) will then also be very large. The same approach as just outlined for a time-dependent gas pressure boundary can be used to realize other time-dependent Dirichlet conditions, such as prescribed temporal variation of temperature, capillary pressure, and others.

For time-independent Dirichlet boundary conditions, TMVOC offers an alternative and more elegant implementation, which provides savings in computational work along with added user conveniences in running simulation problems. This is accomplished with the simple device of "active" and "inactive" elements. By convention, elements encountered in data block "ELEME" (or in geometry files MESH or MINC) are taken to be active until the first element entry with a zero or negative volume is encountered. The first element with volume less than or equal to zero, and all subsequent elements, are by convention taken to be inactive. For the inactive elements no mass or energy balance equations are set up, their primary thermodynamic variables are not included in the list of unknowns, and their thermodynamic conditions will remain unchanged. Inactive elements can appear in flow connections and initial condition specifications like all other elements. The computational overhead of inactive elements is small because they do not increase the number of equations to be solved in a flow problem. The easiest way to declare selected grid blocks inactive is to use a text editor to move them to the end of the ELEME data block, and then insert a dummy grid block of zero volume in front of them.

8.3 Sinks and Sources

Sinks and sources are introduced through data block GENER in the input file. Several options are available for specifying the production ($q < 0$) or injection ($q > 0$) of fluids and heat. Any of the mass components may be injected in an element at a constant rate, or at time-dependent rates that may be prescribed through user-defined tables. The specific enthalpy of the injected fluid may be specified by the user as either a constant or time dependent value. Heat sources/sinks (with no mass injection) may be either constant or time-dependent.

Fluid production from an element may be handled by prescribing a constant or time-dependent mass rate. In this case, the phase composition of the produced fluid may be determined by the relative phase mobilities in the source element. Alternatively, the produced phase composition may be specified to be the same as the phase composition in the producing element. In either case, the mole fractions of the components in the produced phases are determined by the corresponding component mole fractions in the producing element. Different options are available for interpolating time-dependent rates from user-supplied tabular data; these may be selected through parameter MOP(12). Users should note that sink and source rates and enthalpies must be given on a mass basis, in units of kg/s, J/kg, and J/s. These are converted internally in TMVOC to mole-based quantities which are used in the calculations.

Deliverability Model

Production wells may operate on deliverability against a prescribed flowing bottomhole pressure, P_{wb}, with a productivity index PI (Coats, 1977). With this option, the production rate of phase β from a grid block with phase pressure $P_\beta > P_{wb}$ is (see Appendix A for notation)

$$q_\beta = \frac{k_{r\beta}}{\mu_\beta} \rho_\beta \cdot PI \cdot (P_\beta - P_{wb}) \qquad (8.3.1).$$

For steady radial flow the productivity index is given by (Coats, 1977; Thomas, 1982)

$$(PI)_l = \frac{2\pi\left(k\,\Delta z_l\right)}{\ln\left(r_e/r_w\right) + s - 1/2} \qquad (8.3.2)$$

Here, Δz_l denotes the layer thickness, $(k\,\Delta z_l)$ is the permeability-thickness product in layer l, r_e is the grid block radius, r_w is the well radius, and s is the skin factor. If the well is producing from a grid block which does not have cylindrical shape, an approximate PI can be computed by using an effective radius

$$r_e = \sqrt{A/\pi} \tag{8.3.3}$$

where A is the grid block area; e.g., $A = \Delta x \bullet \Delta y$ for an areal Cartesian grid. More accurate expressions for specific well patterns and grid block shapes have been given in the literature (e.g., Peaceman, 1977, 1982; Pritchett and Garg, 1980; Coats and Ramesh, 1982; Hadgu et al., 1993).

The rate of production for mass component κ is

$$\hat{q}^{\kappa} = \sum_{\beta} x_{\beta}^{\kappa} q_{\beta} \tag{8.3.4}$$

For wells which are screened in more than one layer (element), the flowing wellbore pressure P_{wb} can be corrected to approximately account for gravity effects according to the depth-dependent flowing density in the wellbore. Assume that the open interval extends from layer $l = 1$ at the bottom to $l = L$ at the top. The flowing wellbore pressure in layer l, $P_{wb,l}$, is obtained from the wellbore pressure in layer $l + 1$ immediately above it by means of the following recursion formula

$$P_{wb,l} = P_{wb,l+1} + \frac{g}{2}\left(\bar{\rho}_l^f \Delta z_l + \bar{\rho}_{l+1}^f \Delta z_{l+1}\right) \tag{8.3.5}$$

Here, g is acceleration of gravity, and $\bar{\rho}_l^f$ is the flowing density in mass units in the tubing opposite layer l. Flowing densities are computed using a procedure given by Coats (private communication, 1982). If wellbore pressure were zero, we would obtain the following volumetric production rate of phase β from layer l.

$$r_{l,\beta} = \left(\frac{k_{r\beta}}{\mu_\beta}\right)_l (PI)_l \, P_{l,\beta} \tag{8.3.6}$$

The total volumetric flow rate of phase β opposite layer l is, for zero wellbore pressure

$$r_{l,\beta}^T = \sum_{m=1}^{l} r_{m,\beta} \tag{8.3.7}$$

From this we obtain an approximate expression for flowing density opposite layer l which can be used in Eq. (8.3.5).

$$\bar{\rho}_l^f = \overline{M} \sum_\beta \rho_{l,\beta} r_{l,\beta}^T \Big/ \sum_\beta r_{l,\beta}^T \tag{8.3.8}$$

Here, $\overline{M}$ is the average molecular weight of the fluid mixture in units of kg/mole. During fluid production or injection, the rate of heat removal or injection is determined by

$$\hat{q}^h = \sum_\beta q_\beta h_\beta \tag{8.3.9}$$

where h_β is the specific enthalpy of phase β.

8.4 Heat Exchange with Confining Beds

One possible approach for modeling heat exchange with confining beds is to simply extend the computational grid into the cap- and base-rock, which would be given small or vanishing permeability. This way heat exchange would be treated no different than flow in the reservoir. A drawback of this approach is that even for modest accuracy requirements, the number of grid blocks in the heat flow domain could easily become comparable to, or even larger than, the number of grid blocks in the reservoir, leading to a very inefficient calculation. A much more efficient alternative is application of a semi-analytical method, which requires no grid blocks outside of the fluid flow domain, and permits better accuracy for short- and long-term heat exchange. TMVOC provides an option to use the method of Vinsome and Westerveld (1980), which gives excellent accuracy for heat exchange between reservoir fluids and confining beds such as may arise in geothermal injection and production operations.

Observing that the process of heat conduction tends to dampen out temperature variations, Vinsome and Westerveld suggested that cap- and base-rock temperatures would vary smoothly even for strong and rapid temperature changes at the boundary of the conduction zone. Arguing that heat conduction perpendicular to the conductive boundary is more important than parallel to it, they proposed to represent the temperature profile in a semi-infinite conductive layer by means of a simple trial function, as follows:

$$T(x,t) - T_i = \left(T_f - T_i + px + qx^2\right) \exp(-x/d) \tag{8.4.1}$$

Here x is the distance from the boundary, T_i is initial temperature in cap-or base-rock (assumed uniform), T_f is the time-varying temperature at the cap- or base-rock boundary, p and q are time-varying fit parameters, and d is the penetration depth for heat conduction, given by

$$d = \sqrt{\Theta t}/2 \qquad (8.4.2)$$

where $\Theta = K/(\rho C)$ is the thermal diffusivity, K the thermal conductivity, ρ the density of the medium, and C the specific heat. In the context of a finite-difference simulation of nonisothermal flow, each grid block in the top and bottom layers of the computational grid will have an associated temperature profile in the adjacent impermeable rock as given by Eq. (8.4.1). The coefficients p and q will be different for each grid block; they are determined concurrently with the flow simulation from the physical constraints of (1) continuity of heat flux across the boundary, and (2) energy conservation for the reservoir/confining layer system.

There is no separate input data block for specifying a semi-analytical heat exchange calculation. Instead, a number of parameters have to be specified in different blocks to engage this option, as follows. A semi-analytical heat loss calculation will be performed only when the parameter MOP(15) in record PARAM.1 is set equal to 1. Initial temperature as well as heat capacity and conductivity of the confining beds are specified by means of data provided for the very last volume element in data block ELEME. The initial temperature is taken as the temperature with which the last element is initialized. Heat capacity and conductivity are taken from data provided in block ROCKS for the particular domain to which the last element belongs. Thus, if a semi-analytical heat exchange calculation is desired, the user would append an additional inactive element in block ELEME, and provide the desired parameters as initial conditions and domain data, respectively, for this element. Finally, it is necessary to specify which elements have an interface area with the confining beds, and to give the magnitude of this interface area. This information is input as parameter AHTX in columns 31-40 of volume element data in block ELEME. Volume elements for which a zero-interface area is specified will not be subject to heat exchange.

At the termination of a run the data necessary for continuing the heat exchange calculation in a TMVOC continuation run are written onto a disk file TABLE. When restaring a problem, this file has to be provided under the name TABLE. If file TABLE is absent, TMVOC assumes that no prior heat exchange with confining beds has taken place, and takes their temperatures to be uniform and equal to the temperature of the very last volume element in block ELEME. An example of the application of a semi-analytical treatment for heat exchange is given in sample problem 3 of the TOUGH2 V 2.0 user's guide (Pruess et al., 1999).

8.5 Block-by-block Permeability Modification

Heterogeneous flow systems may be specified by providing domains with different hydrogeologic properties, and associating different grid blocks with different domains. In addition, TMVOC provides a feature that applies permeability modification (PM) coefficients for individual grid blocks according to

$$k_n \rightarrow k_n' = k_n \cdot \zeta_n \tag{8.5.1}$$

Here, k_n is the absolute ("reference") permeability of grid block n, as specified in data block ROCKS for the domain to which that grid block belongs, while ζ_n is the permeability modification coefficient. The strength of capillary pressure will be automatically scaled according to (Leverett, 1941)

$$P_{cap,n} \rightarrow P_{cap,n}' = P_{cap,n} / \sqrt{\zeta_n} \tag{8.5.2}$$

Permeability modifiers are initialized by a subroutine PMIN which is called in RFILE after all MESH data have been processed. To engage block-by-block permeability modification, users need to specify a (dummy) domain named 'SEED' in block ROCKS. No grid blocks should be assigned to this domain; the presence of domain 'SEED' simply serves as a flag to put permeability modification into effect, while data provided in domain 'SEED' serve to select different options. Random (spatially uncorrelated) PM data can be internally generated in TMVOC. Alternatively, externally defined permeability modifiers may be provided as part of the geometry data in block ELEME. This feature can be used to apply spatially correlated fields: users can run their own geostatistical package to generate whatever fields they desire, and then use a preprocessing program to place the PM-coefficients into the ELEME data block.

Note that as presently implemented the block-by-block permeability modification affects only grid block permeabilities but not porosities. Full details on the various user options for PM-coefficients are given in informative printout that is automatically generated with each TMVOC run.

8.6 Linear Equation Solvers

The computational work to be performed in the course of a TMVOC simulation includes evaluation of thermophysical properties for all grid blocks, assembly of the vector of residuals and the Jacobian matrix, and solution of the linear equation system for each Newton-Raphson iteration step. Except for small problems with just a few grid blocks, the most computationally intensive of these different tasks is the solution of the linear equation system. TMVOC offers a choice of direct or iterative methods for linear equation solution; technical details of the methods and their performance can be found in (Moridis and Pruess, 1998).

The most reliable linear equation solvers are based on direct methods, while the performance of iterative techniques tends to be problem-specific and lacks the predictability of direct solvers. The robustness of direct solvers comes at the expense of large storage requirements and execution times that typically increase with problem size N (= number of equations solved) proportional to N^3. In contrast, iterative solvers have much lower memory requirements, and their computational work will increase much less rapidly with problem size, approximately proportional to N^{ω}, with $\omega \approx 1.4$ - 1.6 (Moridis and Pruess, 1995). For large problems and especially 3-D problems with several thousand grid blocks or more, iterative conjugate gradient (CG) type solvers are therefore the method of choice.

The default linear equation solution technique in TMVOC uses DSLUCS, a Lanczos-type bi-conjugate gradient solver, with incomplete LU-factorization as preconditioner. Users need to beware that iterative methods can be quite "fickle" and may fail for matrices with special features, such as many zeros on the main diagonal, large numerical range of matrix elements, and nearly linearly dependent rows or columns. Depending on features of the problem at hand, appropriate matrix preconditioning may be essential to achieve convergence. Poor accuracy of the linear equation solution will lead to deteriorated convergence rates for the Newtonian iteration, and an increase in the number of iterations for a given time step. In severe cases, time steps may fail with residuals either stagnating or wildly fluctuating. Information on the convergence of the linear equation solution is written to disk file LINEQ, which may be examined with any text editor. Users experiencing difficulties with the default settings are encouraged to experiment with the various solvers and preconditioners included in the TMVOC package.

The different linear equation solvers included in the TMVOC package can be selected by means of parameter MOP(21) in data record PARAM.1, as follows.

MOP(21) = 1: direct solver MA28
MOP(21) = 2: DSLUBC, a bi-conjugate gradient solver
MOP(21) = 3: DSLUCS, a Lanczos-type bi-conjugate gradient solver
MOP(21) = 4: DSLUGM, a generalized minimum residual solver
MOP(21) = 5: DLUSTB, a stabilized bi-conjugate gradient solver
MOP(21) = 6: direct solver LUBAND

All iterative solvers selected by means of MOP(21) use incomplete LU-factorization as a preconditioner. Alternative preconditioners and iteration parameters can be selected by means of an optional data block SOLVR in the TMVOC input file. If SOLVR is present, its specifications will override the choices made by MOP(21). The default preconditioning with SOLVR is also incomplete LU-factorization. The SOLVR block includes a single data record, as follows.

SOLVR keyword to introduce a data block with parameters for linear equation solvers.

Record SOLVR.1

Format(I1,2X,A2,3X,A2,2E10.4)
MATSLV, ZPROCS, OPROCS, RITMAX, CLOSUR

MATSLV selects the linear equation solver

1: MA28
2: DSLUBC
3: DSLUCS
4: DSLUGM
5: DLUSTB
6: LUBAND

ZPROCS selects the Z-preconditioning (Moridis and Pruess, 1998). Regardless of user specifications, Z-preprocessing will only be performed when iterative solvers are used ($2 \leq$ MATSLV ≤ 5), and if there are zeros on the main diagonal of the Jacobian matrix.

Z0: no Z-preprocessing (default for NEQ=1)
Z1: replace zeros on the main diagonal by a small constant (1.e-25; default for NEQ $\neq$ 1))
Z2: make linear combinations of equations for each grid block to achieve non-zeros on the main diagonal
Z3: normalize equations, followed by Z2

Z4: affine transformation to unit main-diagonal submatrices, without center pivoting

OPROCS selects the O-preconditioning (Moridis and Pruess, 1998).

O0: no O-preprocessing (default, also invoked for NEQ=1)

O1: eliminate lower half of the main-diagonal submatrix with center pivoting

O2: O1, plus eliminate upper half of the main-diagonal submatrix with center pivoting

O3: O2, plus normalize, resulting in unit main-diagonal submatrices

O4: affine transformation to unit main-diagonal submatrices, without center pivoting

RITMAX selects the maximum number of CG iterations as a fraction of the total number of equations ($0.0 < \text{RITMAX} \leq 1.0$; default is RITMAX = 0.1)

CLOSUR convergence criterion for the CG iterations
($1.e\text{-}12 \leq \text{CLOSUR} \leq 1.e\text{-}6$; default is CLOSUR = 1.e-6)

DLUSTB implements the BiCGSTAB(m) algorithm (Sleijpen and Fokkema, 1993), an extension of the BiCGSTAB algorithm of van der Vorst (1992). This has been found to be quite robust, and especially provides improved convergence behavior when iterations are started close to the solution, i.e., near steady state. The preconditoning algorithms can cope with difficult problems in which many of the Jacobian matrix elements on the main diagonal are zero, as often happens in multi-component flow problems where not all components are present in all grid blocks.

9. Output from TMVOC

TMVOC produces a variety of printed output, most of which can be controlled by the user. Information written in the initialization phase to the standard output file includes PARAMETER settings in the main program for dimensioning of problem-size dependent arrays, and disk files in use. This is followed by documentation on block-by-block permeability modification, on settings of the MOP-parameters for choosing program options, and on the EOS-module. During execution TMVOC can optionally generate a brief printout for Newtonian iterations and time steps, as well as messages related to the appearance/disappearance of fluid phases. Using the option MOP(7)>0, the input data can be printed out. Standard output at user-specified simulation times or time steps is generated by a subroutine OUT (each EOS module comes with its own routine OUT). This output provides some time-stepping information, and a complete element-by-element report of thermodynamic state variables and other important parameters. Additional optional output is available on mass and heat flow rates and velocities, and on diffusive fluxes of components in phases. Changes in thermodynamic state variables during a time step may also be printed. Volume and mole balances for the fluid phases as well as mole balances for single mass components in the different phases are printed out by subroutine BALLA. Examples of TMVOC-output are reproduced in section 10, most of which should be self-explanatory. Here we summarize the main output parameters in alphabetical order.

DELTEX	time step size, seconds
Dgas	gas phase density, kg/m^3
DNAPL	NAPL (oil phase) density, kg/m^3
DT	time step size, seconds
DX1, DX2, etc.	changes in first, second, etc. thermodynamic variable
DX1M, DX2M, DX3M	maximum change in first, second, and third primary variable in current time step
ELEM	code name of element
ELEM1, ELEM2	code name of first and second element, respectively, in a flow connection
ENTHALPY	flowing specific enthalpy for mass sinks/sources, J/kg
FF(GAS), FF(Aq), FF(NAPL)	mole fraction of flow in gas, aqueous, and NAPL phases, respectively (mass production wells only)
FFVOC(GAS), FFVOC(Aq)	total VOC mole fraction of flow in gas and aqueous phases, respectively (mass production wells only)
FLOF	total rate of fluid flow, mole/s (positive if from ELEM2 into ELEM1)
FLO(GAS)	total rate of gas flow, mole/s (positive if from ELEM2 into ELEM1)

FLOH	total rate of heat flow, W (positive if from ELEM2 into ELEM1)
FLO(Aq)	total rate of aqueous phase flow, mole/s (positive if from ELEM2 into ELEM1)
FLO(NAPL)	total rate of NAPL phase flow, mole/s (positive if from ELEM2 into ELEM1)
FLO(VOC)Aq	total rate of VOC flow in aqueous phase, mole/s (positive if fromELEM2 into ELEM1)
FLO(VOC)GAS	total rate of VOC flow in gas phase, mole/s (positive if fromELEM2 into ELEM1)
GENERATION RATE	sink (> 0) or source (< 0) rate, kg/s (mass), W (heat)
INDEX	internal indexing number of elements, connections, sinks/sources
ITER	number of Newtonian iterations in current time step
ITERC	total cumulative number of Newtonian iterations in simulation run
H Aq	Aqueous phase enthalpy (J/mole)
H gas	Gas phase enthalpy (J/mole)
H NAPL	NAPL enthalpy (J/mole)
KCYC	time step counter
KER	index number of equation with largest residual
KRgas	gas phase relative permeability
KR Aq	aqueous phase relative permeability
KRoil	NAPL phase relative permeability
KON	convergence flag; KON = 2: converged; KON = 1: not converged
MAX. RES.	maximum (relative) residual in any of the mass and energy balance equations (see Eq. B.8)
NER	index number of element (grid block) with largest residual
P	pressure, Pa
PCwg	capillary pressure between the gas-aqueous phases, Pa
PCog	capillary pressure between the gas-NAPL phases, Pa
PWB	flowing bottomhole pressure (production wells on deliverability only), Pa
SG	gas saturation
SW	aqueous phase saturation
SO	NAPL saturation
SOURCE	code name of sink/source
ST	simulation time, in seconds

SUMmolef	{sum of component mole fractions in a phase} - 1
T	temperature, ℃
TOTAL TIME	simulation time, in seconds
VAPDIF	diffusive vapor flow rate, kg/s (positive if from ELEM2 into ELEM1)
VEL(GAS)	gas phase pore velocity, m/s (positive if from ELEM2 into ELEM1)
VEL(WAT)	aqueous phase pore velocity, m/s (positive if from ELEM2 into ELEM1)
VEL(NAPL)	NAPL pore velocity, m/s (positive if from ELEM2 into ELEM1)
VIS Aq	aqueous phase viscosity, Pa-s
VISGAS	gas phase viscosity, Pa-s
VISOIL	NAPL viscosity, Pa-s
X1, X2, etc.	first, second, etc. thermodynamic variable (also: water 1, water 2)
XVOCw	total mass fraction of VOCs in the aqueous phase
Xwat	mole fraction of water in the different phases
Z-factor	real gas compressibility factor

Time series of some parameters for plotting can optionally be written to files FOFT (for elements), COFT (for connections), and GOFT (for sinks and sources). These files are written in subroutine FGTAB, called from and following CYCIT. At present there are no input options to select the parameters to be written out in FGTAB; users desiring different parameters than what is coded in FGTAB should modify that subroutine.

10. Sample Problems

In this section we present and discuss a number of sample problems for TMVOC which can serve as a tutorial for TMVOC applications and as benchmarks for proper code installation. Our emphasis is on demonstrating preparation of input data and illustrating code capabilities. Accordingly, most of the problems consist of small and often coarse grid systems. Users are reminded that, for accurate solution to flow problems, careful attention needs to be given to issues of space discretization and time step control. Numerous verification and validation exercises performed with various TOUGH2 modules are available in separate reports (e.g., Moridis and Pruess, 1992, 1995; Pruess et al., 1996). These demonstrate that the code can obtain accurate solutions to physically and mathematically well-posed problems, and can successfully describe laboratory experiments and field observations on fluid flow and heat transfer processes. TMVOC has been extensively cross-checked against other TOUGH2 modules. Comparisons with T2VOC are given in some of the sample problems below.

In addition to their primary purpose of documenting and benchmarking code applications, the input data files can also be used as templates to facilitate preparation of input data for new flow problems. We envisage that a user rarely if ever will assemble a new input file from scratch; instead (s)he will modify an existing input file to suit a new application.

In the data records for keywords (such as ROCKS, PARAM, etc.) in TMVOC input files, only the first 5 characters are read. As seen in the input files for the sample problems, below, we have adopted a convention of writing column counters following the keywords. This is done as a convenience to facilitate alignment of the fixed-format data with data fields.

Users are cautioned that for problems that involve (dis-)appearance of phases or components, the numerical performance can be quite sensitive to subtle issues of floating point accuracy and numerical roundoff. The sample problems given below were executed on an IBM RS/6000 workstation under the AIX Version 4 operating system. On different computing platforms the time stepping sequence may be somewhat different, so that final results also may be somewhat different due to different time truncation errors. The most sensitive check for proper code installation is provided by the quantities printed as "MAX. RES." in the output file, which represent the maximum relative difference, for all grid blocks and equations, between the left-hand sides (accumulation terms) and right-hand sides (flow terms) of the governing equations. During the Newton-Raphson iteration process these residuals are reduced to smaller and smaller values, until they drop below specified convergence tolerances. As convergence is approached, the residuals are subject to increasingly severe numerical cancellation, arising from subtracting two numbers with

diminishing difference. Small differences due to roundoff will first show up in different values for the “MAX. RES.”, long before giving any visible changes in primary variables or their increments.

10.1 Problem No. 1 (*r7c*) - Demonstrating Initialization of Different Phase Conditions

Here we present an input file (Fig. 10.1.1) and portions of the TMVOC printout (Fig. 10.1.2) generated from it to document the initialization of different phase conditions. A single infinitesimal time step of 1.e-9 s was specified, and no flow simulation is carried out. Note that mole fractions for all components are assigned to the PAR array for all phases (and are printed in the output file) even when not all phases are present. As discussed in Appendix D, this is done to permit a treatment of molecular diffusion that is fully coupled with phase partitioning under multiphase conditions.

Users should note that the proper initialization of multiphase multicomponent systems can be difficult because of several thermodynamic constraints acting simultaneously. We envision that 2 or 3-phase conditions that include a NAPL will rarely be initialized directly; instead, a flow simulation will typically be started from single-phase water (saturated zone) or two-phase water-gas conditions (unsaturated zone) without any VOC present. VOC distributions and the possible evolution of a NAPL phase would then be computed using appropriate injection specifications to simulate a contamination event (see sections 10.4, 10.5, and 10.7).

TMVOC checks user-specified initial conditions during the initialization phase. Any thermodynamic inconsistencies encountered will be noted in informative messages, and will cause the simulation run to stop.

```
*r7c* ... testing all initializations; no data block NCGAS (defaults NCG=1, air)
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SANDA    2     2650.       .360   1.0e-11   1.0e-11   1.0e-11       2.1     720.0
    1.0E-8                          0.25
    6           .150        .05        .01        3.
    8          0.000       1.84        10.       11.

CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
BENZENE 1
     562.2      48.2     0.271     0.212       0.0
     353.2  -6.98273   1.33213  -2.62863  -3.33399
    78.114-.3392E+020.4739E+00-.3017E-030.7130E-07
      885.    289.00 0.770E-05    273.10      1.52
0.4612E+010.1489E+03-.2544E-010.2222E-04     259.0
 0.411E-03 0.000E+00 0.000E+00 0.000E+00
 0.891E-01     0.001
n-DECANE
   617.700    21.200     0.249     0.489      0.00
   447.300  -8.56523   1.97756  -5.81971  -0.29982
   142.286 -7.913E+0  9.609E-1 -5.288E-4  1.131E-7
   730.000   293.000  1.000E-5   293.000     1.600
                      0.5900   293.000   603.000
  3.799e-7
     0.000
..... ie(2)=1 choose SRK; ie(3)=1 choose Khair = 1.E10 Pa, as in EOS3 and T2VOC
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1    1

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    4    5    3    6
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   4   1       1100090  0000 004  0 0000
       0.0                 -1.
     1.e-9
     1.e-5       1.0                                  1.e-8
    6
           0.1013e6                  .55              .44974                   .5
                20.
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
G  01         1SANDA       1.0
W  02         1SANDA       1.0
N  03         1SANDA       1.0
WG 04         1SANDA       1.0
NG 05         1SANDA       1.0
WN 06         1SANDA       1.0
WGN07         1SANDA       1.0
def06         1SANDA       1.0

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----

INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
G  01    0    0                1
            0.1013e6                1.e-8               1.e-8                0.99
                20.
W  02    0    0                2
            0.1013e6                1.e-8               1.e-8               1.e-8
                20.
N  03    0    0                3
            0.1013e6                  0.5                 0.5               1.e-6
                20.
WG 04    0    0                4
            0.1013e6                1.e-8               1.e-8                 0.5
                20.
NG 05    0    0                5
            0.1013e6               .09730               1.e-8                 0.5
                20.
WN 06    0    0                6
            0.1013e6                  0.5                 0.5                 0.5
                20.
WGN07    0    0                7
            0.1013e6                  0.3               1.e-8                 0.2
                20.

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.1.1. TMVOC input file for initialization test.

```
*r7c* ... testing all initializations; no data block NCGAS (defaults NCG=1, air)

         OUTPUT DATA AFTER (   1,  1)-2-TIME STEPS                                                
```

10.2 Problem No. 2 (*rblm*) - 1-D Buckley-Leverett Flow

Here we present an adaptation of T2VOC sample problem no. 2 to TMVOC. The flow system is initialized in two-phase water-NAPL conditions, with a water saturation of 15.9 % so that NAPL (chlorobenzene) saturation is 84.1 %. The input file as shown in Fig. 10.2.1 is very similar to the T2VOC input file for this problem. An NCGAS data block with a single non-condensible gas (AIR) was included, although this is not required in this case because the choices made in NCGAS are TMVOC defaults. Portions of the printed output are shown in Fig. 10.2.2. The results agree very closely with those from T2VOC.

```
*rblm* ... Buckley/Leverett problem for TMVOC: inject water into chlorobenzene
MESHMAKER1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
XYZ
       00.
NX      40      7.62
NX       1
       0.0
NY       1       1.0
NZ       1       1.0


ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
DIRT1    1    1.E+20       .20  2.96E-13  2.96E-13  2.96E-13       3.1     1000.
     1.e-8

CHEMP----1----*-Modified Chlorobenzene data-*----5----*----6----*----7----*----8
    1
CHLOROBENZENE
     632.4      45.2     0.265     0.249       1.6
     404.9    -7.587   2.26551  -4.09418   0.17038
   112.559    -33.89     .5631 -4.522E-4  1.426E-7
     998.3    292.15    8.0E-6    273.15      1.00
        0.        0.       1.0    292.15      308.
    1.0E-7        0.        0.        0.
        0.        0.        0.
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
AIR
..... ie(2)=1 choose SRK; ie(3)=1 choose KHair = 1.E10 Pa, as in EOS3 and T2VOC
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1    1

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    3    3    3    6
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   4 200     200100000000 00000300001000
           1.296E+8       -1.   8.64E+5              9.8060
     1.e+3
     1.E-5     1.E00                                1.000e-8
    6
            6.895E5                  1.               0.159                19.0
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   11
    9
GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A11 1INJ 1                        COM1   150.6e-6     80.e3

INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A1141                      .2 6
            6.895E5                 1.0                0.80                19.0

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.2.1. Input file for sample problem 2 (Buckley-Leverett).

```
********** VOLUME- AND MASS-BALANCES **********************************************************************************************

********** [KCYC,ITER] = [   0,  0] *****                                  THE TIME IS   .00000E+00 SECONDS, OR   .00000E+00 DAYS

PHASES                      GAS            AQUEOUS           NAPL            TOTAL

VOLUMES     (m**3)     .00000000E+00     .96926400E+01     .51267360E+02     .60960000E+02
MASS       (moles)     .00000000E+00     .53735172E+06     .45523189E+06     .99258362E+06
ENERGY         (J)     .00000000E+00     .77096530E+09     .11474721E+10     .46329600E+27

                        COMPONENTS MOLES IN PLACE - BY PHASES                                COMPONENTS IN PLACE - OVERALL

COMPONENTS              GAS PHASE       AQUEOUS PHASE          NAPL           ADSORBED         TOTAL MOLES     TOTAL MASS (kg)
WATER                  .00000000E+00     .53735167E+06     .10873734E+03                     .53746041E+06     .96828867E+04
AIR                    .00000000E+00     .00000000E+00     .00000000E+00                     .00000000E+00     .00000000E+00
CHLOROBENZENE          .00000000E+00     .53722337E-01     .45512316E+06     .00000000E+00     .45512321E+06     .51228213E+05
total VOCs             .00000000E+00     .53722337E-01     .45512316E+06     .00000000E+00     .45512321E+06     .51228213E+05
**********************************************************************************************************************************


...ITERATING...  AT [   1,  1] --- DELTEX =  .100000E+04   MAX. RES. =  .622129E-03  AT ELEMENT A11 1  EQUATION   1
A11 1(   1,  2) ST =  .100000E+04 DT =  .100000E+04 DX1=  .472480E+04 DX2= -.238861E-03 T =  19.000 P =   694225. S =  .000000E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+04   MAX. RES. =  .124346E-02  AT ELEMENT A11 1  EQUATION   1
A11 1(   2,  2) ST =  .300000E+04 DT =  .200000E+04 DX1=  .556933E+04 DX2=  .000000E+00 T =  19.000 P =   699794. S =  .000000E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+04   MAX. RES. =  .248381E-02  AT ELEMENT A11 1  EQUATION   1
A11 1(   3,  2) ST =  .700000E+04 DT =  .400000E+04 DX1=  .709877E+04 DX2=  .000000E+00 T =  19.000 P =   706893. S =  .000000E+00
...ITERATING...  AT [   4,  1] --- DELTEX =  .800000E+04   MAX. RES. =  .495530E-02  AT ELEMENT A11 1  EQUATION   1
A11 1(   4,  2) ST =  .150000E+05 DT =  .800000E+04 DX1=  .954002E+04 DX2=  .000000E+00 T =  19.000 P =   716433. S =  .000000E+00
...ITERATING...  AT [   5,  1] --- DELTEX =  .160000E+05   MAX. RES. =  .986169E-02  AT ELEMENT A11 1  EQUATION   1
A11 1(   5,  2) ST =  .310000E+05 DT =  .160000E+05 DX1=  .131696E+05 DX2=  .000000E+00 T =  19.000 P =   729602. S =  .000000E+00
...ITERATING...  AT [   6,  1] --- DELTEX =  .320000E+05   MAX. RES. =  .195306E-01  AT ELEMENT A11 1  EQUATION   1
A11 1(   6,  2) ST =  .630000E+05 DT =  .320000E+05 DX1=  .184157E+05 DX2=  .000000E+00 T =  19.000 P =   748018. S =  .000000E+00
...ITERATING...  AT [   7,  1] --- DELTEX =  .640000E+05   MAX. RES. =  .383107E-01  AT ELEMENT A11 1  EQUATION   1
...ITERATING...  AT [   7,  2] --- DELTEX =  .640000E+05   MAX. RES. =  .140571E-04  AT ELEMENT A11 1  EQUATION   1
A11 2(   7,  3) ST =  .127000E+06 DT =  .640000E+05 DX1=  .256067E+05 DX2=  .000000E+00 T =  19.000 P =   767886. S =  .000000E+00
...ITERATING...  AT [   8,  1] --- DELTEX =  .128000E+06   MAX. RES. =  .737768E-01  AT ELEMENT A11 1  EQUATION   1
...ITERATING...  AT [   8,  2] --- DELTEX =  .128000E+06   MAX. RES. =  .587701E-04  AT ELEMENT A11 1  EQUATION   1
A11 2(   8,  3) ST =  .255000E+06 DT =  .128000E+06 DX1=  .350714E+05 DX2=  .000000E+00 T =  19.000 P =   802957. S =  .000000E+00
...ITERATING...  AT [   9,  1] --- DELTEX =  .256000E+06   MAX. RES. =  .137272E+00  AT ELEMENT A11 1  EQUATION   1
...ITERATING...  AT [   9,  2] --- DELTEX =  .256000E+06   MAX. RES. =  .333354E-03  AT ELEMENT A11 1  EQUATION   1
A11 2(   9,  3) ST =  .511000E+06 DT =  .256000E+06 DX1=  .427444E+05 DX2=  .000000E+00 T =  19.000 P =   845701. S =  .000000E+00
...ITERATING...  AT [  10,  1] --- DELTEX =  .512000E+06   MAX. RES. =  .240323E+00  AT ELEMENT A11 1  EQUATION   1
...ITERATING...  AT [  10,  2] --- DELTEX =  .512000E+06   MAX. RES. =  .313396E-02  AT ELEMENT A11 2  EQUATION   1
A11 2(  10,  3) ST =  .102300E+07 DT =  .512000E+06 DX1=  .400943E+05 DX2=  .000000E+00 T =  19.000 P =   885796. S =  .000000E+00
...ITERATING...  AT [  11,  1] --- DELTEX =  .864000E+06   MAX. RES. =  .320574E+00  AT ELEMENT A11 1  EQUATION   1
...ITERATING...  AT [  11,  2] --- DELTEX =  .864000E+06   MAX. RES. =  .186668E-01  AT ELEMENT A11 2  EQUATION   1
...ITERATING...  AT [  11,  3] --- DELTEX =  .864000E+06   MAX. RES. =  .108291E-04  AT ELEMENT A11 1  EQUATION   1
A11 2(  11,  4) ST =  .188700E+07 DT =  .864000E+06 DX1=  .237980E+05 DX2=  .000000E+00 T =  19.000 P =   909594. S =  .000000E+00
...ITERATING...  AT [  12,  1] --- DELTEX =  .864000E+06   MAX. RES. =  .225869E+00  AT ELEMENT A11 1  EQUATION   1
...ITERATING...  AT [  12,  2] --- DELTEX =  .864000E+06   MAX. RES. =  .166410E-01  AT ELEMENT A11 2  EQUATION   1
...ITERATING...  AT [  12,  3] --- DELTEX =  .864000E+06   MAX. RES. =  .449347E-04  AT ELEMENT A11 2  EQUATION   1
A11 2(  12,  4) ST =  .275100E+07 DT =  .864000E+06 DX1=  .869918E+04 DX2=  .000000E+00 T =  19.000 P =   918293. S =  .000000E+00
...ITERATING...  AT [  13,  1] --- DELTEX =  .864000E+06   MAX. RES. =  .160826E+00  AT ELEMENT A11 1  EQUATION   1
...ITERATING...  AT [  13,  2] --- DELTEX =  .864000E+06   MAX. RES. =  .857466E-02  AT ELEMENT A11 2  EQUATION   1
...ITERATING...  AT [  13,  3] --- DELTEX =  .864000E+06   MAX. RES. =  .262738E-04  AT ELEMENT A11 2  EQUATION   1
A11 3(  13,  4) ST =  .361500E+07 DT =  .864000E+06 DX1=  .290764E+04 DX2=  .000000E+00 T =  19.000 P =   914525. S =  .000000E+00
...ITERATING...  AT [  14,  1] --- DELTEX =  .864000E+06   MAX. RES. =  .145845E+00  AT ELEMENT A11 2  EQUATION   1
...ITERATING...  AT [  14,  2] --- DELTEX =  .864000E+06   MAX. RES. =  .410478E-02  AT ELEMENT A11 3  EQUATION   1
A11 2(  14,  3) ST =  .447900E+07 DT =  .864000E+06 DX1=  .204810E+04 DX2=  .000000E+00 T =  19.000 P =   923969. S =  .000000E+00
```

Figure 10.2.2. Part of printed output for sample problem 2.

```
*rblm* ... Buckley/Leverett problem for TMVOC: inject water into chlorobenzene

         OUTPUT DATA AFTER (  159,  3)-2-TIME STEPS                                                
```

10.3 Problem No. 3 (*rdif2*) - Diffusion

This problem examines diffusion of several solutes (air, benzene, and n-decane) in single-phase water and is similar to sample problem *rdif7* from TOUGH2, Version 2.0 (Pruess et al., 1999). A 1-D grid of 20 blocks is initialized in single-phase aqueous conditions, with no solutes present. Boundary conditions provided by an inactive (zero volume; see section 8.2) grid block "ina 1" include step changes of 1.e-7, 1.e-8, and 1.e-6, respectively, for mole fractions of benzene, n-decane, and air. Also, there is a 1 °C change of temperature at the boundary. All diffusivities are specified as -1.e-6 m^2/s (see Fig. 10.3.1), where the "-" sign serves as a switch to suppress tortuosity effects (see Appendix D). Diffusivities are equal to 1.e-6 m^2/s for all mass components, and thermal parameters were chosen in such a way that thermal diffusivity $\Theta = K/\rho C$ also has the same value. Advective processes are suppressed by setting permeabilities to zero. For the same step change in the diffusing quantity (temperature for thermal diffusion, mole fractions for mass diffusion) at the boundary, all diffusive profiles should then be identical. The step changes imposed here differ by powers of 10, and apart from these factors the simulated diffusive profiles are seen to be identical (Fig. 10.3.2).

```
*rdif2* ... 1-D diffusion problem for water
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SANDY    2     2500.     1.e-4    0.e-12    0.e-12    0.e-12       2.5     1000.
     1.e-8                           0.25           0.00e-04  0.00E-00
    1            0.        0.        1.        1.
    9

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    4    5    3    8
CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
BENZENE
     562.2      48.2     0.271     0.212       0.0
     353.2  -6.98273   1.33213  -2.62863  -3.33399
    78.114-.3392E+020.4739E+00-.3017E-030.7130E-07
      885.    289.00 0.770E-05    273.10      1.52
                        0.5900   293.000     259.0
 0.415E-03 0.000E+00 0.000E+00 0.000E+00
 0.891E-01     0.001
n-DECANE
   617.700    21.200     0.249     0.489      0.00
   447.300  -8.56523   1.97756  -5.81971  -0.29982
   142.286 -7.913E+0  9.609E-1 -5.288E-4  1.131E-7
   730.000   293.000  1.000E-5   293.000     1.600
                        0.5900   293.000   603.000
  3.799e-7
     0.000
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
AIR
..... ie(2)=1 choose SRK; ie(3)=1 choose Khair = 1.E10 Pa, as in EOS3 and T2VOC
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1    1

START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   4  30      301000 0  0000 004  0 0000
       0.0   .1427e7       -1.      1.e5
      1.e3
     1.e-8     1.e-3                                    1.e-8
    2
                 1.e5              0.e-7              0.e-8              0.e-6
                   8.
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    -1.e-6    -1.e-6
    -1.e-6    -1.e-6
    -1.e-6    -1.e-6
    -1.e-6    -1.e-6
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A   1   19    1    1        .1
ina 1

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----
ina 1A   1                   1     1.e-9       .05        1.
A   1A   2   18    1    1    1       .05       .05        1.

INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
ina 1                          2
                 1.e5              1.e-7              1.e-8              1.e-6
                   9.

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.3.1. Input file for sample problem 3 (diffusion).

```
...ITERATING...  AT [   1,  1] --- DELTEX =  .100000E+04   MAX. RES. =  .249983E-01  AT ELEMENT A   1  EQUATION   5
...ITERATING...  AT [   1,  2] --- DELTEX =  .100000E+04   MAX. RES. =  .272024E-06  AT ELEMENT A   1  EQUATION   1
A   1(   1,  3) ST =  .100000E+04 DT =  .100000E+04 DX1=  .816579E+03 DX2=  .154845E-07 T =   8.155 P =   100817. S =  .000000E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+04   MAX. RES. =  .379744E-01  AT ELEMENT A   1  EQUATION   5
...ITERATING...  AT [   2,  2] --- DELTEX =  .200000E+04   MAX. RES. =  .300083E-06  AT ELEMENT A   1  EQUATION   1
A   1(   2,  3) ST =  .300000E+04 DT =  .200000E+04 DX1=  .110339E+04 DX2=  .199595E-07 T =   8.354 P =   101920. S =  .000000E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+04   MAX. RES. =  .477807E-01  AT ELEMENT A   1  EQUATION   5
...ITERATING...  AT [   3,  2] --- DELTEX =  .400000E+04   MAX. RES. =  .302193E-06  AT ELEMENT A   1  EQUATION   1
A   2(   3,  3) ST =  .700000E+04 DT =  .400000E+04 DX1=  .565541E+03 DX2=  .106170E-07 T =   8.167 P =   100885. S =  .000000E+00
...ITERATING...  AT [   4,  1] --- DELTEX =  .800000E+04   MAX. RES. =  .469317E-01  AT ELEMENT A   1  EQUATION   5
...ITERATING...  AT [   4,  2] --- DELTEX =  .800000E+04   MAX. RES. =  .183332E-06  AT ELEMENT A   2  EQUATION   1
A   1(   4,  3) ST =  .150000E+05 DT =  .800000E+04 DX1=  .939469E+03 DX2=  .154855E-07 T =   8.710 P =   104027. S =  .000000E+00
...ITERATING...  AT [   5,  1] --- DELTEX =  .160000E+05   MAX. RES. =  .375411E-01  AT ELEMENT A   2  EQUATION   5
...ITERATING...  AT [   5,  2] --- DELTEX =  .160000E+05   MAX. RES. =  .205222E-06  AT ELEMENT A   2  EQUATION   1
A   2(   5,  3) ST =  .310000E+05 DT =  .160000E+05 DX1=  .950901E+03 DX2=  .165510E-07 T =   8.489 P =   102697. S =  .000000E+00
...ITERATING...  AT [   6,  1] --- DELTEX =  .320000E+05   MAX. RES. =  .389930E-01  AT ELEMENT A   2  EQUATION   5
...ITERATING...  AT [   6,  2] --- DELTEX =  .320000E+05   MAX. RES. =  .184739E-06  AT ELEMENT A   3  EQUATION   1
A   4(   6,  3) ST =  .630000E+05 DT =  .320000E+05 DX1=  .774496E+03 DX2=  .141565E-07 T =   8.285 P =   101532. S =  .000000E+00
...ITERATING...  AT [   7,  1] --- DELTEX =  .640000E+05   MAX. RES. =  .378766E-01  AT ELEMENT A   3  EQUATION   5
...ITERATING...  AT [   7,  2] --- DELTEX =  .640000E+05   MAX. RES. =  .184295E-06  AT ELEMENT A   4  EQUATION   1
A   6(   7,  3) ST =  .127000E+06 DT =  .640000E+05 DX1=  .706148E+03 DX2=  .130280E-07 T =   8.245 P =   101305. S =  .000000E+00
...ITERATING...  AT [   8,  1] --- DELTEX =  .100000E+06   MAX. RES. =  .290463E-01  AT ELEMENT A   4  EQUATION   5
...ITERATING...  AT [   8,  2] --- DELTEX =  .100000E+06   MAX. RES. =  .134550E-06  AT ELEMENT A   6  EQUATION   1
A   9(   8,  3) ST =  .227000E+06 DT =  .100000E+06 DX1=  .525363E+03 DX2=  .979632E-08 T =   8.188 P =   100998. S =  .000000E+00
...ITERATING...  AT [   9,  1] --- DELTEX =  .100000E+06   MAX. RES. =  .157680E-01  AT ELEMENT A   6  EQUATION   5
...ITERATING...  AT [   9,  2] --- DELTEX =  .100000E+06   MAX. RES. =  .652991E-07  AT ELEMENT A   7  EQUATION   1
A   7(   9,  3) ST =  .327000E+06 DT =  .100000E+06 DX1=  .503502E+03 DX2=  .889667E-08 T =   8.391 P =   102127. S =  .000000E+00
...ITERATING...  AT [  10,  1] --- DELTEX =  .100000E+06   MAX. RES. =  .106028E-01  AT ELEMENT A   7  EQUATION   5
...ITERATING...  AT [  10,  2] --- DELTEX =  .100000E+06   MAX. RES. =  .353683E-07  AT ELEMENT A   8  EQUATION   1
A   9(  10,  3) ST =  .427000E+06 DT =  .100000E+06 DX1=  .370322E+03 DX2=  .661579E-08 T =   8.336 P =   101816. S =  .000000E+00
...

 *rdif2* ... 1-D diffusion problem for water

         OUTPUT DATA AFTER (  20,  3)-2-TIME STEPS                                                    THE TIME IS   .16516E+02 DAYS
@@@
```

```
        *rdif2* ... 1-D diffusion problem for water

                                                                                KCYC =   20  -  ITER =    3  -  TIME =  .14270E+07

                                    >>>>>>>>>> MOLE FRACTIONS IN THE AQUEOUS PHASE <<<<<<<<

ELEM. INDEX   Xwat      2 AIR       3 BENZENE   4 n-DECANE ** SUMmolef
A   1   2   .10000E+01  .97865E-06  .97865E-07  .97865E-08  .00000E+00
A   2   2   .10000E+01  .93608E-06  .93608E-07  .93608E-08  .00000E+00
A   3   2   .10000E+01  .89393E-06  .89393E-07  .89393E-08  .00000E+00
A   4   2   .10000E+01  .85244E-06  .85244E-07  .85244E-08  .00000E+00
A   5   2   .10000E+01  .81189E-06  .81189E-07  .81189E-08  .00000E+00
A   6   2   .10000E+01  .77254E-06  .77254E-07  .77254E-08  .00000E+00
A   7   2   .10000E+01  .73462E-06  .73462E-07  .73462E-08  .00000E+00
A   8   2   .10000E+01  .69837E-06  .69837E-07  .69837E-08  .00000E+00
A   9   2   .10000E+01  .66402E-06  .66402E-07  .66402E-08  .00000E+00
A  10   2   .10000E+01  .63178E-06  .63178E-07  .63178E-08  .00000E+00
A  11   2   .10000E+01  .60183E-06  .60183E-07  .60183E-08  .00000E+00
A  12   2   .10000E+01  .57436E-06  .57436E-07  .57436E-08  .00000E+00
A  13   2   .10000E+01  .54953E-06  .54953E-07  .54953E-08  .00000E+00
A  14   2   .10000E+01  .52748E-06  .52748E-07  .52748E-08  .00000E+00
A  15   2   .10000E+01  .50835E-06  .50835E-07  .50835E-08  .00000E+00
A  16   2   .10000E+01  .49223E-06  .49223E-07  .49223E-08  .00000E+00
A  17   2   .10000E+01  .47923E-06  .47923E-07  .47923E-08  .00000E+00
A  18   2   .10000E+01  .46942E-06  .46942E-07  .46942E-08  .00000E+00
A  19   2   .10000E+01  .46284E-06  .46284E-07  .46284E-08  .00000E+00
A  20   2   .10000E+01  .45955E-06  .45955E-07  .45955E-08  .00000E+00
ina 1   2   .10000E+01  .10000E-05  .10000E-06  .10000E-07  .00000E+00
```

Figure 10.3.2. Part of printed output for sample problem 3 (continued).

10.4 Problem No. 4 (*rtcem*) - Steam Displacement of a NAPL in a Laboratory Column

This problem is an adaptation of T2VOC sample problem no. 3 (Falta et al., 1995). It models, in a somewhat simplified way, a laboratory experiment conducted by Hunt et al. (1988). The simulation consists of three parts that involve, respectively, injection, waterflooding, and steamflooding of TCE in a horizontal sandpacked column. The column is 91 cm long with a cross sectional area of 20.428 cm^2. The mesh used for this simulation consists of 50 evenly spaced elements with a mesh spacing of 1.82 cm. Initially, the column is water saturated with no air or VOC present.

The first part of the simulation involves the injection of liquid trichloroethylene into a system that is in single-phase liquid (aqueous) conditions and is run with the input file shown in Fig. 10.4.1. We specify NKIN = -2 in data block MULTI to initialize the system with two-component (water and air) T2VOC-style initial conditions. This is done to illustrate use of this option; further explanations are given in Appendix E. The temperature in the column is 22 °C, and deliverability boundary conditions are used at each end of the column. The deliverability boundary condition is specified by setting TYPE in record GENER.1 equal to `DELV` and by specifying a productivity index (GX in record GENER.1) and a wellbore pressure (EX in record GENER.1). Trichloroethylene is injected at a constant rate into the 15th element by choosing the `COM3` option for TYPE in record GENER.1. The specific enthalpy of the injected trichloroethylene (EX in record GENER.1) corresponds to liquid trichloroethylene at a temperature of about 22 °C. Because the TCE injection is run in isothermal mode (NEQ=NK=3 in MULTI) this enthalpy specification is not really necessary. The various constants used to compute the thermophysical properties of trichloroethylene are contained in data block CHEMP. Details of the three-phase relative permeability functions (IRP = 6 in record RPCAP.1) and the three-phase capillary pressure functions (ICP = 8 in record RPCAP.2) may be found in Appendices G and H, respectively.

Trichloroethylene is injected into the column for a period of 120 s, with an initial time step size of 2 seconds. A partial printout of the T2VOC simulation results is given in Figure 10.4.2; agreement with the T2VOC simulation of the same problem is excellent (Falta et al., 1995; pp. 84 - 87). The NAPL plume (region with SO $\neq$ 0) is seen to extend from grid block AA 12 to AA 18.

The second part of this simulation consists of injecting cold water (22 °C) into one end of the column and allowing fluids to drain from the other end of the column according to a deliverability boundary condition (TYPE = `DELV` in record GENER.1). The initial conditions for this part of the simulation are the conditions at the end of the first part of the simulation. To start the

second part of the simulation, the SAVE file generated by the first part of the simulation was placed into the input file, shown (partly) in Figure 10.4.3. This file is otherwise similar to the previous input file (Figure 10.4.1), except that data block GENER has been changed. These changes consist of removing the NAPL injection, and changing the inlet condition at the first element to water (COM1) injection. Water with a specific enthalpy of 9.2332 x 10^4 J/kg is injected at a rate of 3.5395 x 10^{-4} kg/s (a Darcy velocity of 15 m/day) for a period of 17,880 s with an initial time step size of 2 s. The simulation is run to a total time of 18,000 s (120 s + 17,880 s), and a partial printout of results is given in Figure 10.4.4. The NAPL plume has migrated downstream and spread. It extends from grid block AA 18 to AA 32 but has not reached the outlet. The aqueous phase downstream from the plume contains VOC at a mole fraction of .15091e-3, corresponding to the solubility limit of 1.100 kg/m^3. 24.6 % of the original VOC has been removed by dissolution in the aqueous phase and subsequent extraction from well PRO 1. The results agree well with the T2VOC simulation (Falta et al., 1995; pp. 90 - 93).

The final part of the simulation consists of steam injection into the column. Again, the initial conditions for this part of the problem are the conditions at the end of the previous part. The file SAVE generated during the waterflood part of the simulation was placed in the input file as block INCON (Fig. 10.4.5). During this final part of the simulation, steam with an enthalpy of 1.562xl0^6 J/kg is injected at a rate of 3.5341x10^{-5} kg/s for a period of 9000 s. Parameter NEQ in MULTI is increased to 4, to include an energy balance equation, and printout is specified for a total time of 23,000 s (5000 s after start of steam injection) using data block TIMES.

Part of the output is shown in Figure 10.4.6. After 5,000 s of steam injection, a compact NAPL bank is present in the condensation zone ahead of the steam front (grid blocks AA 39 to AA 43), demonstrating that the steam is effectively displacing the trichloroethylene. By the end of the simulation, after 9000 s of steam injection, the entire column is at the steam temperature, and the trichloroethylene has been completely removed. Simulation results agree well with those from a T2VOC simulation, but TMVOC requires a considerably larger number of time steps for this problem (779 vs. 520 for T2VOC).

The reason why a TMVOC simulation may proceed somewhat differently from T2VOC is in significant differences in the treatment of thermodynamic conditions. For example, TMVOC calculates gas phase density and specific enthalpy from the cubic SRK equation of state (Redlich and Kwong, 1949; Soave, 1972), while T2VOC uses an ideal gas mixture assumption. The aqueous phase is not allowed to disappear in T2VOC, while TMVOC allows all possible phase

combinations in the gas-water-NAPL system. TMVOC includes effects of water dissolution in the NAPL, which were neglected in T2VOC.

To illustrate the use of multiple non-condensible gases, we also present a variation of the steamflooding problem in which oxygen and nitrogen are selected in data block NCGAS instead of air. The problem is again run in three segments, first NAPL injection, then waterflood, followed by steamflood. Here we only show the steamflood portion which is run with the input file given in Fig. 10.4.7. There now are NK=4 fluid components (water, O_2, N_2, TCE), and NEQ=5 equations to solve. The INCON-data generated by the waterflood have 5 primary variables. This problem is quite difficult in terms of the linear equation solution, because O_2 and N_2 concentrations are close to zero at all times, and the Jacobian matrix has a large and variable number of zero elements on the main diagonal. The run proceeds somewhat differently from the version with air, which is due to differences in the Jacobian matrix, and consequent differences in the linear equation solution and convergence of the Newtonian iterations during time stepping. Fig. 10.4.8 shows that a simulation time of 23,000 s is reached after 592 time steps (591 time steps for the problem with air), and the total number of Newtonian iterations up to this time is ITERC=4333 (4230 for the problem with air). The results are close but not identical to the air problem (compare Figs. 10.4.6 and 10.4.8). The final simulation time of 27,000 s is reached after 788 time steps in the O_2 + N_2 problem (not shown), as compared to 779 time steps for the problem with air. The accuracy of the linear equation solution depends on the number of significant digits available for the floating point operations. Accordingly, the convergence rate of the Newtonian iterations and the time stepping sequence may be somewhat different on different computing platforms.

```
*rtcem1*  TMVOC: INJECTION OF TRICHLOROETHYLENE INTO A COLUMN; nkin=-2
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
DIRT1    1     2650.      .385   1.6E-11   1.6E-11   1.6E-11       3.1     1000.
     0.e-8        0.      2.85       0.0

CHEMP----1----*-trichloroethylene data-4----*----5----*----6----*----7----*----8
    1
TCE
     572.0      50.5     0.265     0.213       0.9
     360.4  -7.38190   1.94817  -3.03294  -5.34536
   131.389    30.170     .2287-2.229E-04 8.244E-08
     1462.     293.0   8.0E-06     273.0      1.60
        0.        0.      0.59    293.15     256.0
1.50954E-4        0.        0.        0.
        0.        0.        0.
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
AIR
..... ie(2)=1 choose SRK; ie(3)=1 choose Kh air = 1.E10 Pa, as in EOS3 and T2VOC
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1    1

..... nkin= -2 : a T2VOC incon format is used !!!
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    3    3    3    6   -2
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   4  20      20100030000000002 4 0001000
              120.00        2.      120.              9.8060
     1.E-5     1.E00
            1.0133e5                50.0                22.0
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .150       .05      .001        3.
    8          0.000      1.84       10.       11.
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1   49    1DIRT1 3.7179E-5

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1AA  2   48    1    1    1     .0091     .0091 2.0428E-3       0.0

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1end 1                         DELV 3.5917E-12 1.0140E+5
AA 50end 2                         DELV 3.5917E-12 1.0140E+5
AA 15INO 1                         COM3 2.1900E-04 2.2100E+4

INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.4.1. TMVOC input file for part 1 of problem 4 (TCE injection).

```
********** VOLUME- AND MASS-BALANCES **********************************************************************************************

********** [KCYC,ITER] = [   0,  0] *****                                  THE TIME IS   .00000E+00 SECONDS, OR   .00000E+00 DAYS

PHASES                      GAS             AQUEOUS           NAPL             TOTAL

VOLUMES     (m**3)     .00000000E+00     .71571500E-03     .00000000E+00     .71571500E-03
MASS       (moles)     .00000000E+00     .39642773E+02     .00000000E+00     .39642773E+02
ENERGY         (J)     .00000000E+00     .65860914E+05     .00000000E+00     .13251443E+06


                        COMPONENTS MOLES IN PLACE - BY PHASES                                COMPONENTS IN PLACE - OVERALL

COMPONENTS              GAS PHASE       AQUEOUS PHASE          NAPL            ADSORBED         TOTAL MOLES     TOTAL MASS (kg)
WATER                  .00000000E+00     .39642773E+02     .00000000E+00                     .39642773E+02     .71420419E+00
AIR                    .00000000E+00     .39642773E-28     .00000000E+00                     .39642773E-28     .11480547E-29
TCE                    .00000000E+00     .39642773E-28     .00000000E+00     .00000000E+00   .39642773E-28     .52086242E-29
total VOCs             .00000000E+00     .39642773E-28     .00000000E+00     .00000000E+00   .39642773E-28     .52086242E-29
**************************************************************************************************************************************


...ITERATING...  AT [   1,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .896614E+02  AT ELEMENT AA 15  EQUATION   3
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 15*  $$$   xsumoil=   .27854E+02
...ITERATING...  AT [   1,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .487960E+03  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   1,  3] --- DELTEX =  .200000E+01   MAX. RES. =  .349026E+00  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   1,  4] --- DELTEX =  .200000E+01   MAX. RES. =  .599881E-01  AT ELEMENT AA 15  EQUATION   3
AA 14(   1,  5) ST =  .200000E+01 DT =  .200000E+01 DX1=  .834697E+03 DX2=  .221151E-05 T =  22.000 P =   102165. S =  .000000E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .100000E+01  AT ELEMENT AA 15  EQUATION   3
...ITERATING...  AT [   2,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .993583E-02  AT ELEMENT AA 16  EQUATION   3
AA 14(   2,  3) ST =  .400000E+01 DT =  .200000E+01 DX1= -.497742E+00 DX2=  .217747E-05 T =  22.000 P =   102164. S =  .000000E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+01   MAX. RES. =  .100000E+01  AT ELEMENT AA 15  EQUATION   3
...ITERATING...  AT [   3,  2] --- DELTEX =  .400000E+01   MAX. RES. =  .868339E+00  AT ELEMENT AA 14  EQUATION   3
...ITERATING...  AT [   3,  3] --- DELTEX =  .400000E+01   MAX. RES. =  .548189E-03  AT ELEMENT AA 14  EQUATION   3
AA 16(   3,  4) ST =  .800000E+01 DT =  .400000E+01 DX1=  .448500E+01 DX2=  .354609E-04 T =  22.000 P =   102207. S =  .000000E+00
...ITERATING...  AT [   4,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .174515E+01  AT ELEMENT AA 14  EQUATION   3
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 14*  $$$   xsumoil=   .24565E+01
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 16*  $$$   xsumoil=   .22508E+01
...ITERATING...  AT [   4,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .170533E+02  AT ELEMENT AA 14  EQUATION   3
...ITERATING...  AT [   4,  3] --- DELTEX =  .800000E+01   MAX. RES. =  .400315E+00  AT ELEMENT AA 14  EQUATION   3
...ITERATING...  AT [   4,  4] --- DELTEX =  .800000E+01   MAX. RES. =  .188117E+00  AT ELEMENT AA 14  EQUATION   3
...ITERATING...  AT [   4,  5] --- DELTEX =  .800000E+01   MAX. RES. =  .116356E-04  AT ELEMENT AA 13  EQUATION   3
AA 14(   4,  6) ST =  .160000E+02 DT =  .800000E+01 DX1=  .552903E+02 DX2=  .999671E+00 T =  22.000 P =   102218. S =  .000000E+00
...ITERATING...  AT [   5,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .947765E+00  AT ELEMENT AA 16  EQUATION   3
...ITERATING...  AT [   5,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .836650E+00  AT ELEMENT AA 14  EQUATION   3
...ITERATING...  AT [   5,  3] --- DELTEX =  .800000E+01   MAX. RES. =  .463972E-02  AT ELEMENT AA 16  EQUATION   3
AA 16(   5,  4) ST =  .240000E+02 DT =  .800000E+01 DX1=  .891963E+02 DX2=  .867467E-17 T =  22.000 P =   102363. S =  .000000E+00
...ITERATING...  AT [   6,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .148976E+01  AT ELEMENT AA 16  EQUATION   3
...ITERATING...  AT [   6,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .169305E+01  AT ELEMENT AA 13  EQUATION   3
...ITERATING...  AT [   6,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .685332E-02  AT ELEMENT AA 17  EQUATION   3
...ITERATING...  AT [   6,  4] --- DELTEX =  .160000E+02   MAX. RES. =  .114795E-03  AT ELEMENT AA 13  EQUATION   3
AA 17(   6,  5) ST =  .400000E+02 DT =  .160000E+02 DX1=  .204501E+02 DX2=  .469361E-04 T =  22.000 P =   102227. S =  .000000E+00
...ITERATING...  AT [   7,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .858301E+00  AT ELEMENT AA 17  EQUATION   3
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 13*  $$$   xsumoil=   .24970E+01
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 17*  $$$   xsumoil=   .15928E+01
...ITERATING...  AT [   7,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .844044E+01  AT ELEMENT AA 13  EQUATION   3
...ITERATING...  AT [   7,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .379179E+00  AT ELEMENT AA 12  EQUATION   3
...ITERATING...  AT [   7,  4] --- DELTEX =  .160000E+02   MAX. RES. =  .299669E+00  AT ELEMENT AA 12  EQUATION   3
...ITERATING...  AT [   7,  5] --- DELTEX =  .160000E+02   MAX. RES. =  .442518E-04  AT ELEMENT AA 12  EQUATION   3
AA 13(   7,  6) ST =  .560000E+02 DT =  .160000E+02 DX1=  .558531E+02 DX2=  .999623E+00 T =  22.000 P =   102146. S =  .000000E+00
...ITERATING...  AT [   8,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .892987E+00  AT ELEMENT AA 17  EQUATION   3
...ITERATING...  AT [   8,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .119320E+01  AT ELEMENT AA 17  EQUATION   3
...ITERATING...  AT [   8,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .981495E-02  AT ELEMENT AA 12  EQUATION   3
AA 17(   8,  4) ST =  .720000E+02 DT =  .160000E+02 DX1=  .869572E+02 DX2=  .172947E-16 T =  22.000 P =   102369. S =  .000000E+00
...ITERATING...  AT [   9,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .155414E+01  AT ELEMENT AA 17  EQUATION   3
...ITERATING...  AT [   9,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .812437E+01  AT ELEMENT AA 12  EQUATION   3
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 12*  $$$   xsumoil=   .27329E+01
...ITERATING...  AT [   9,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .691830E+01  AT ELEMENT AA 12  EQUATION   3
...ITERATING...  AT [   9,  4] --- DELTEX =  .320000E+02   MAX. RES. =  .911254E+00  AT ELEMENT AA 12  EQUATION   3
...ITERATING...  AT [   9,  5] --- DELTEX =  .320000E+02   MAX. RES. =  .435052E-02  AT ELEMENT AA 12  EQUATION   3
AA 12(   9,  6) ST =  .104000E+03 DT =  .320000E+02 DX1=  .281942E+02 DX2=  .999678E+00 T =  22.000 P =   102054. S =  .000000E+00
...ITERATING...  AT [  10,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .456032E+00  AT ELEMENT AA 12  EQUATION   3
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 18*  $$$   xsumoil=   .21644E+01
...ITERATING...  AT [  10,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .213490E+01  AT ELEMENT AA 18  EQUATION   3
...ITERATING...  AT [  10,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .192649E+00  AT ELEMENT AA 19  EQUATION   3
...ITERATING...  AT [  10,  4] --- DELTEX =  .160000E+02   MAX. RES. =  .148269E+00  AT ELEMENT AA 19  EQUATION   3
...ITERATING...  AT [  10,  5] --- DELTEX =  .160000E+02   MAX. RES. =  .241716E-04  AT ELEMENT AA 19  EQUATION   3
AA 18(  10,  6) ST =  .120000E+03 DT =  .160000E+02 DX1=  .507413E+02 DX2=  .999570E+00 T =  22.000 P =   102304. S =  .000000E+00
```

Figure 10.4.2. Portion of printed output for part 1 of problem 4.

```
*rtcem1*  TMVOC: INJECTION OF TRICHLOROETHYLENE INTO A COLUMN; nkin=-2

         OUTPUT DATA AFTER (  10,  6)-2-TIME STEPS                                                    THE TIME IS   .13889E-02 DAYS
@@@
```

```
*rtcem2*  TMVOC: WATERFLOODING OF TCE
...
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    3    3    3    6
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   3 100     10010003000000002 4 00 1 00
           18000.00        2.     8000.              9.8060
     1.E-5     1.E02                                1.000e-8               1.e+4
    2
           1.0133e5                0.00                  0.0                22.0
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6          .150       .05      .001        3.
    8          0.000      1.84      10.       11.
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1   49    1DIRT1 3.7179E-5

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1AA  2   48    1    1    1     .0091     .0091 2.0428E-3       0.0

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA 50PRO 1                        DELV 3.5917E-12 1.0140E+5
AA  1INJ 1                        COM1 3.5395E-04 9.2332E+4

INCON -- INITIAL CONDITIONS FOR   50 ELEMENTS AT TIME   .120000E+03
...
AA  9            .38500000E+00 2
  .1018524107567E+06  .2433400175293E-05  .1903102196660E-20  .2200000000000E+02
AA 10            .38500000E+00 2
  .1019056354619E+06  .1103762602867E-04  .1561998416009E-19  .2200000000000E+02
AA 11            .38500000E+00 2
  .1019588601641E+06  .4549057460679E-04  .4805850495739E-19  .2200000000000E+02
AA 12            .38500000E+00 6
  .1020937919145E+06  .9997160425154E+00  .9944385452780E+00  .2200000000000E+02
AA 13            .38500000E+00 6
  .1026300850715E+06  .9997160425154E+00  .8617005434031E+00  .2200000000000E+02
AA 14            .38500000E+00 6
  .1032175152789E+06  .9997160425154E+00  .6905600449084E+00  .2200000000000E+02
AA 15            .38500000E+00 6
  .1036455795090E+06  .9997160425154E+00  .5953854222830E+00  .2200000000000E+02
AA 16            .38500000E+00 6
  .1032812082392E+06  .9997160425154E+00  .7091031666517E+00  .2200000000000E+02
AA 17            .38500000E+00 6
  .1027431349188E+06  .9997160425154E+00  .8959250792547E+00  .2200000000000E+02
AA 18            .38500000E+00 6
  .1023035699155E+06  .9997160425154E+00  .9985791865696E+00  .2200000000000E+02
AA 19            .38500000E+00 2
  .1022396278775E+06  .2302169668704E-04  .9433747639043E-20  .2200000000000E+02
AA 20            .38500000E+00 2
  .1022129730149E+06  .2812045633888E-05  .1498389392053E-20  .2200000000000E+02
...
ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.4.3. Portion of TMVOC input file for part 2 of problem 4 (waterflood).

```
********** VOLUME- AND MASS-BALANCES **********************************************************************************************

********** [KCYC,ITER] = [  10,  0] *****                                  THE TIME IS   .12000E+03 SECONDS, OR   .13889E-02 DAYS

PHASES                      GAS             AQUEOUS           NAPL             TOTAL

VOLUMES     (m**3)     .00000000E+00     .69776046E-03     .17954541E-04     .71571500E-03
MASS       (moles)     .00000000E+00     .38645285E+02     .19931828E+00     .38844604E+02
ENERGY         (J)     .00000000E+00     .64203702E+05     .54472341E+03     .13140194E+06

                        COMPONENTS MOLES IN PLACE - BY PHASES                              COMPONENTS IN PLACE - OVERALL

COMPONENTS              GAS PHASE       AQUEOUS PHASE          NAPL            ADSORBED         TOTAL MOLES     TOTAL MASS (kg)
WATER                  .00000000E+00     .38644530E+02     .56597916E-04                     .38644587E+02     .69622088E+00
AIR                    .00000000E+00     .22076827E-18     .00000000E+00                     .22076827E-18     .63934491E-20
trichloroethylene      .00000000E+00     .75506629E-03     .19926168E+00     .00000000E+00     .20001674E+00     .26280000E-01
total VOCs             .00000000E+00     .75506629E-03     .19926168E+00     .00000000E+00     .20001674E+00     .26280000E-01
**********************************************************************************************************************************


...ITERATING...  AT [  11,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .635470E-01  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [  11,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .787199E-01  AT ELEMENT AA 15  EQUATION   1
...ITERATING...  AT [  11,  3] --- DELTEX =  .200000E+01   MAX. RES. =  .922957E-02  AT ELEMENT AA 13  EQUATION   3
AA 14(  11,  4) ST =  .122000E+03 DT =  .200000E+01 DX1=  .746738E+04 DX2= -.375255E-13 T =  22.000 P =   110685. S =  .000000E+00
...ITERATING...  AT [  12,  1] --- DELTEX =  .400000E+01   MAX. RES. =  .177039E+00  AT ELEMENT AA 17  EQUATION   3
...ITERATING...  AT [  12,  2] --- DELTEX =  .400000E+01   MAX. RES. =  .553724E-02  AT ELEMENT AA 18  EQUATION   3
...ITERATING...  AT [  12,  3] --- DELTEX =  .400000E+01   MAX. RES. =  .119886E-04  AT ELEMENT AA 18  EQUATION   1
AA 16(  12,  4) ST =  .126000E+03 DT =  .400000E+01 DX1=  .807766E+02 DX2= -.145627E-23 T =  22.000 P =   109417. S =  .000000E+00
...ITERATING...  AT [  13,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .311447E+00  AT ELEMENT AA 17  EQUATION   3
...ITERATING...  AT [  13,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .399986E-01  AT ELEMENT AA 18  EQUATION   3
...ITERATING...  AT [  13,  3] --- DELTEX =  .800000E+01   MAX. RES. =  .253569E-03  AT ELEMENT AA 18  EQUATION   1
AA 18(  13,  4) ST =  .134000E+03 DT =  .800000E+01 DX1=  .538391E+02 DX2= -.666365E-24 T =  22.000 P =   107648. S =  .000000E+00
...ITERATING...  AT [  14,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .538006E+00  AT ELEMENT AA 18  EQUATION   3
...ITERATING...  AT [  14,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .103672E+00  AT ELEMENT AA 18  EQUATION   3
...ITERATING...  AT [  14,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .101210E-02  AT ELEMENT AA 18  EQUATION   1
AA 18(  14,  4) ST =  .150000E+03 DT =  .160000E+02 DX1=  .132995E+03 DX2= -.218650E-22 T =  22.000 P =   107781. S =  .000000E+00
...ITERATING...  AT [  15,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .141132E+01  AT ELEMENT AA 18  EQUATION   3
...ITERATING...  AT [  15,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .156855E+00  AT ELEMENT AA 18  EQUATION   1
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 19*  $$$   xsumoil=   .29845E+01
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 20*  $$$   xsumoil=   .14502E+01
...ITERATING...  AT [  15,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .114380E+00  AT ELEMENT AA 19  EQUATION   3
$$$ 6 ---> 2 $$$ NAPL DISAPP. AT ELEMENT *AA 20*  $$$   SW =   .10006E+01
...ITERATING...  AT [  15,  4] --- DELTEX =  .320000E+02   MAX. RES. =  .382755E+00  AT ELEMENT AA 19  EQUATION   1
...ITERATING...  AT [  15,  5] --- DELTEX =  .320000E+02   MAX. RES. =  .362771E-03  AT ELEMENT AA 19  EQUATION   1
AA 19(  15,  6) ST =  .182000E+03 DT =  .320000E+02 DX1=  .528090E+02 DX2=  .999631E+00 T =  22.000 P =   107397. S =  .000000E+00
...ITERATING...  AT [  16,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .623643E+00  AT ELEMENT AA 18  EQUATION   3
...ITERATING...  AT [  16,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .184713E+00  AT ELEMENT AA 19  EQUATION   1
...ITERATING...  AT [  16,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .824815E-02  AT ELEMENT AA 19  EQUATION   1
AA 20(  16,  4) ST =  .214000E+03 DT =  .320000E+02 DX1= -.932603E-03 DX2=  .285188E-04 T =  22.000 P =   107155. S =  .000000E+00
...ITERATING...  AT [  17,  1] --- DELTEX =  .640000E+02   MAX. RES. =  .911142E+00  AT ELEMENT AA 19  EQUATION   3
...ITERATING...  AT [  17,  2] --- DELTEX =  .640000E+02   MAX. RES. =  .673629E+00  AT ELEMENT AA 19  EQUATION   1
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 20*  $$$   xsumoil=   .15301E+01
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 21*  $$$   xsumoil=   .11333E+01
...ITERATING...  AT [  17,  3] --- DELTEX =  .640000E+02   MAX. RES. =  .396655E-01  AT ELEMENT AA 20  EQUATION   3
$$$ 6 ---> 2 $$$ NAPL DISAPP. AT ELEMENT *AA 21*  $$$   SW =   .10004E+01
...ITERATING...  AT [  17,  4] --- DELTEX =  .640000E+02   MAX. RES. =  .438022E+00  AT ELEMENT AA 20  EQUATION   1
...ITERATING...  AT [  17,  5] --- DELTEX =  .640000E+02   MAX. RES. =  .252314E-03  AT ELEMENT AA 20  EQUATION   1
AA 20(  17,  6) ST =  .278000E+03 DT =  .640000E+02 DX1=  .283100E+02 DX2=  .999601E+00 T =  22.000 P =   107183. S =  .000000E+00
...ITERATING...  AT [  18,  1] --- DELTEX =  .640000E+02   MAX. RES. =  .756571E+00  AT ELEMENT AA 19  EQUATION   3
...ITERATING...  AT [  18,  2] --- DELTEX =  .640000E+02   MAX. RES. =  .362639E+00  AT ELEMENT AA 20  EQUATION   1
...ITERATING...  AT [  18,  3] --- DELTEX =  .640000E+02   MAX. RES. =  .448281E-01  AT ELEMENT AA 20  EQUATION   1
AA 21(  18,  4) ST =  .342000E+03 DT =  .640000E+02 DX1= -.534559E-03 DX2=  .177565E-04 T =  22.000 P =   106966. S =  .000000E+00
...ITERATING...  AT [  19,  1] --- DELTEX =  .128000E+03   MAX. RES. =  .860547E+00  AT ELEMENT AA 19  EQUATION   3
...ITERATING...  AT [  19,  2] --- DELTEX =  .128000E+03   MAX. RES. =  .190439E+01  AT ELEMENT AA 20  EQUATION   1
...ITERATING...  AT [  19,  3] --- DELTEX =  .128000E+03   MAX. RES. =  .427483E-01  AT ELEMENT AA 21  EQUATION   1
...ITERATING...  AT [  19,  4] --- DELTEX =  .128000E+03   MAX. RES. =  .108332E-04  AT ELEMENT AA 20  EQUATION   1
AA 13(  19,  5) ST =  .470000E+03 DT =  .128000E+03 DX1= -.791147E+02 DX2= -.327054E-20 T =  22.000 P =   110200. S =  .000000E+00
```

Figure 10.4.4. Portion of printed output for part 2 of problem 4.

```
 *rtcem2*  TMVOC: WATERFLOODING OF TCE

          OUTPUT DATA AFTER (  41,  4)-2-TIME STEPS                                                    THE TIME IS   .20833E+00 DAYS
@@@
```

```
*rtcem3*  TMVOC: STEAMFLOODING OF A TCE BANK
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
DIRT1    1     2650.      .385   1.6E-11   1.6E-11   1.6E-11       3.1     1000.
     0.e-8        0.      2.85       0.0

...
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    3    4    3    6
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
 9 31999    1999100030000000002 4 00 2 00
           27000.00       -1.     2000.              9.8060
       20.
     1.E-5     1.E02                                 1.e-06               1.e+4
    2
           1.0133e5                0.00                 0.0                22.0
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .150       .05      .001        3.
   10          0.000      1.84       10.       11.
TIMES----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
     23.e3
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1   49    1DIRT1 3.7179E-5

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1AA  2   48    1    1    1     .0091     .0091 2.0428E-3       0.0

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA 50PRO 1                        DELV 3.5917E-12 1.0140E+5
AA  1INJ 1                        COM1 3.5341E-05   1.562e6

INCON -- INITIAL CONDITIONS FOR   50 ELEMENTS AT TIME   .180000E+05
AA  1            .38500000E+00 2
  .1114636655744E+06  .7511555344729E-29  .2895007288839E-51  .2200000000000E+02
AA  2            .38500000E+00 2
  .1112749780662E+06  .8414418922537E-28  .8309693527039E-50  .2200000000000E+02
AA  3            .38500000E+00 2
  .1110862905303E+06  .1096382519643E-28  .1249868398762E-48  .2200000000000E+02
...
AA 16            .38500000E+00 2
  .1086333500363E+06  .1253984052195E-06  .1863308156046E-32  .2200000000000E+02
AA 17            .38500000E+00 2
  .1084446621116E+06  .1157836715725E-04  .9809412498193E-31  .2200000000000E+02
AA 18            .38500000E+00 6
  .1084882999860E+06  .9997160425154E+00  .9635236969712E+00  .2200000000000E+02
AA 19            .38500000E+00 6
  .1083226745125E+06  .9997160425154E+00  .9492034916908E+00  .2200000000000E+02
AA 20            .38500000E+00 6
  .1081011692024E+06  .9997160425154E+00  .9475224954772E+00  .2200000000000E+02
AA 21            .38500000E+00 6
  .1078834980482E+06  .9997160425154E+00  .9441820776929E+00  .2200000000000E+02
```

Figure 10.4.5. Portion of TMVOC input file for part 3 of problem 4.

```
********** VOLUME- AND MASS-BALANCES **********************************************************************************************

********** [KCYC,ITER] = [  41,  0] *****                                    THE TIME IS   .18000E+05 SECONDS, OR   .20833E+00 DAYS

PHASES                      GAS            AQUEOUS           NAPL            TOTAL

VOLUMES     (m**3)     .00000000E+00     .70247801E-03     .13236991E-04     .71571500E-03
MASS       (moles)     .00000000E+00     .38894342E+02     .14694853E+00     .39041291E+02
ENERGY         (J)     .00000000E+00     .64617254E+05     .40155240E+03     .13167232E+06

                        COMPONENTS MOLES IN PLACE - BY PHASES                              COMPONENTS IN PLACE - OVERALL

COMPONENTS              GAS PHASE       AQUEOUS PHASE          NAPL            ADSORBED        TOTAL MOLES     TOTAL MASS (kg)
WATER                  .00000000E+00     .38890497E+02     .41727135E-04                     .38890539E+02     .70065195E+00
AIR                    .00000000E+00     .32338141E-30     .00000000E+00                     .32338141E-30     .93651257E-32
trichloroethylene      .00000000E+00     .38448038E-02     .14690680E+00     .00000000E+00     .15075161E+00     .19807103E-01
total VOCs             .00000000E+00     .38448038E-02     .14690680E+00     .00000000E+00     .15075161E+00     .19807103E-01
**********************************************************************************************************************************


...ITERATING...  AT [  42,  1] --- DELTEX =  .200000E+02   MAX. RES. =  .446173E+00  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [  42,  2] --- DELTEX =  .200000E+02   MAX. RES. =  .115478E+00  AT ELEMENT AA  1  EQUATION   4
...ITERATING...  AT [  42,  3] --- DELTEX =  .200000E+02   MAX. RES. =  .126700E-01  AT ELEMENT AA  2  EQUATION   4
...ITERATING...  AT [  42,  4] --- DELTEX =  .200000E+02   MAX. RES. =  .362258E-04  AT ELEMENT AA  1  EQUATION   4
AA  2(  42,  5) ST =  .180200E+05 DT =  .200000E+02 DX1= -.884237E+04 DX2=  .453810E-16 T =  22.588 P =   102433. S =  .000000E+00
...ITERATING...  AT [  43,  1] --- DELTEX =  .200000E+02   MAX. RES. =  .265826E+00  AT ELEMENT AA  1  EQUATION   4
...ITERATING...  AT [  43,  2] --- DELTEX =  .200000E+02   MAX. RES. =  .131367E-02  AT ELEMENT AA  1  EQUATION   1
AA  2(  43,  3) ST =  .180400E+05 DT =  .200000E+02 DX1=  .810861E+01 DX2= -.224008E-17 T =  23.657 P =   102441. S =  .000000E+00
...ITERATING...  AT [  44,  1] --- DELTEX =  .400000E+02   MAX. RES. =  .396017E+00  AT ELEMENT AA  1  EQUATION   4
...ITERATING...  AT [  44,  2] --- DELTEX =  .400000E+02   MAX. RES. =  .649222E-02  AT ELEMENT AA  1  EQUATION   1
AA  2(  44,  3) ST =  .180800E+05 DT =  .400000E+02 DX1=  .772248E+01 DX2= -.409253E-17 T =  27.104 P =   102448. S =  .000000E+00
...
*rtcem3*  TMVOC: STEAMFLOODING OF A TCE BANK

         OUTPUT DATA AFTER (  591,  4)-2-TIME STEPS                                                    THE TIME IS   .26620E+00 DAYS
@@@
```

```
*rtcem3*  TMVOC: STEAMFLOODING OF A TCE BANK

         OUTPUT DATA AFTER (  779,  3)-2-TIME STEPS                                                    THE TIME IS   .31250E+00 DAYS
@@@
```

```
*rtcem3on* ... TMVOC: STEAMFLOODING OF A TCE BANK; two gases O2+N2
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
DIRT1    1     2650.      .385   1.6E-11   1.6E-11   1.6E-11       3.1     1000.
     0.e-8        0.      2.85       0.0

...
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
O2
N2
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1    0

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    4    5    3    6
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
 9 31999    1999000000000000 4 00 1 00
            27000.00       -1.     2000.              9.8060
       20.
     1.E-5     1.E02                                  1.e-06               1.e+4
    2
            1.0133e5               0.00                 0.0                0.00
                22.0
...
GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA 50PRO 1                        DELV 3.5917E-12 1.0140E+5
AA  1INJ 1                        COM1 3.5341E-05   1.562e6

INCON -- INITIAL CONDITIONS FOR   50 ELEMENTS AT TIME  0.180000E+05
AA  1           0.38500000E+00 2
 0.1114636655746E+06 0.8158296419253E-29 0.1198556210339E-57 0.3028362729482E-50
 0.2200000000000E+02
AA  2           0.38500000E+00 2
 0.1112749780664E+06 0.5118535448057E-28 0.3488757153340E-56 0.7558901557495E-49
 0.2200000000000E+02
...
AA 17           0.38500000E+00 2
 0.1084446621118E+06 0.1157836716945E-04 0.2487581434748E-44 0.9809412499562E-31
 0.2200000000000E+02
AA 18           0.38500000E+00 6
 0.1084882999873E+06 0.9997160425154E+00 0.3274627458466E-44 0.9635236966728E+00
 0.2200000000000E+02
AA 19           0.38500000E+00 6
 0.1083226745125E+06 0.9997160425154E+00 0.9996402142056E-44 0.9492034916908E+00
 0.2200000000000E+02
AA 20           0.38500000E+00 6
 0.1081011692024E+06 0.9997160425154E+00 0.2936987404656E-43 0.9475224954773E+00
 0.2200000000000E+02
AA 21           0.38500000E+00 6
 0.1078834980482E+06 0.9997160425154E+00 0.8267559599359E-43 0.9441820776932E+00
 0.2200000000000E+02
```

Figure 10.4.7. Portion of TMVOC input file for the steamflood in the $O_2 + N_2$ variation of problem 4.

```
********** VOLUME- AND MASS-BALANCES **********************************************************************************************

********** [KCYC,ITER] = [  41,  0] *****                                    THE TIME IS   .18000E+05 SECONDS, OR   .20833E+00 DAYS

PHASES                      GAS             AQUEOUS           NAPL             TOTAL

VOLUMES     (m**3)     .00000000E+00     .70247801E-03     .13236991E-04     .71571500E-03
MASS       (moles)     .00000000E+00     .38894342E+02     .14694853E+00     .39041291E+02
ENERGY         (J)     .00000000E+00     .64617254E+05     .40155240E+03     .13167232E+06

                        COMPONENTS MOLES IN PLACE - BY PHASES                                COMPONENTS IN PLACE - OVERALL

COMPONENTS              GAS PHASE       AQUEOUS PHASE          NAPL            ADSORBED        TOTAL MOLES     TOTAL MASS (kg)
WATER                  .00000000E+00     .38890497E+02     .41727135E-04                     .38890539E+02     .70065195E+00
O2                     .00000000E+00     .73145917E-30     .27511404E-35                     .73146193E-30     .23406050E-31
N2                     .00000000E+00     .14000923E-15     .00000000E+00                     .14000923E-15     .39415624E-17
trichloroethylene      .00000000E+00     .38448038E-02     .14690680E+00     .00000000E+00     .15075161E+00     .19807103E-01
total VOCs             .00000000E+00     .38448038E-02     .14690680E+00     .00000000E+00     .15075161E+00     .19807103E-01

************************************************************************************************************************************


AA  2(  42,  5) ST =  .180200E+05 DT =  .200000E+02 DX1= -.884237E+04 DX2=  .178524E-21 T =  22.588 P =   102433. S =  .000000E+00
AA  2(  43,  3) ST =  .180400E+05 DT =  .200000E+02 DX1=  .810861E+01 DX2= -.178524E-21 T =  23.657 P =   102441. S =  .000000E+00
AA  2(  44,  3) ST =  .180800E+05 DT =  .400000E+02 DX1=  .772248E+01 DX2=  .127930E-17 T =  27.104 P =   102448. S =  .000000E+00
...

*rtcem3on* ... TMVOC: STEAMFLOODING OF A TCE BANK; two gases O2+N2

         OUTPUT DATA AFTER ( 592,  3)-2-TIME STEPS                                                    THE TIME IS   .26620E+00 DAYS
@@@
```

10.5 Problem No. 5 (*rbt*) - Steam Displacement of a Benzene-Toluene Mixture in a Laboratory Column

This is a variation of sample problem no. 4, corresponding to a different experiment of Hunt et al. (1988) in which instead of trichloroethylene a two-component mixture of benzene and toluene was injected over a period of 120 s. The input file as shown in Fig. 10.5.1 is essentially identical to the one for the TCE problem (Fig. 10.4.1), except that (i) CHEMP data were changed to toluene and benzene, (ii) in MULTI we set NK = NEQ = 4 (water, air, toluene, benzene), (iii) initial conditions now require NK+1 = 5 parameters, and (iv) injection specifications were modified. At prevailing conditions of (T, P) = (22 °C, 1.013e5 Pa) the densities of benzene and toluene are, respectiveley, 878.94 and 865.06 kg/m^3. Injection rates were set in such a way that 9 ml of each would be injected in 120 s. Following Adenekan (1992), we also increased the irreducible gas saturation from a value of .001 used in the TCE problem no. 4 to .01. The results of the VOC injection run are generally similar to what was obtained for the TCE problem and are shown, in part, in Fig. 10.5.2.

VOC emplacement is followed again by a waterflood which in this case consists of two parts, a high-rate part in which 9 pore volumes of water are injected at a Darcy velocity of 15 m/day, and a low-rate part in which 1.2 pore volumes are injected at a Darcy velocity of 0.4 m/day. The 15 m/day Darcy velocity corresponds to a volumetric water injection rate of 15*20.428e-4/86400 = 3.5465e-7 m^3/s, which at ambient water density of 997.649 kg/m ^{3} translates into a mass rate of 3.5382e-4 kg/s. This rate is maintained for 18.162e3 seconds, corresponding to injection of 9 pore volumes. Subsequently injection rate is changed to 9.4352e-6 kg/s, corresponding to a Darcy velocity of 0.4 m/day, and injection continues for another 90.809e3 seconds, so that at the final time of 108.971 e3 seconds a total of 10.2 pore volumes have been injected. The SAVE file of the first run segment is used as data block INCON in the input file for waterflooding, part of which is shown in Fig. 10.5.3. Note that we set MOP(12)=2, to rigorously maintain desired total water injection across the step change in water rate after 9 pore volumes, corresponding to t = 18.162e3 s. Fig. 10.5.4. shows part of the printout generated by this run. It is seen that, due to the higher solubility of benzene as compared to toluene, the NAPL plume is depleted of benzene at the upstream end. The mass balances indicate that 81.5 % of the initial benzene inventory of .1013 moles have been removed by the waterflood, while of the initial toluene inventory of .08450 mole only 21.3 % were removed. NAPL phase saturations at the beginning of the waterflood, and after injection of 1.2, 9, and 10.2 pore volumes, are shown in Fig. 10.5.5. Time series of benzene and toluene mole fractions in the aqueous phase at the outlet (grid block AA 50) were generated by means of the FOFT data block, using a modified version of subroutine FGTAB in which the first 5 primary variables are written out, as follows:

```
                do79 j=1,neq5
                xd((i-1)*neq5+j)=x(nloc+j)
79              continue
```

The mole fractions of VOCs were converted to mass fractions according to

$$X^\kappa = \frac{x^\kappa M_\kappa}{\sum_j x^j M_j} \cong x^\kappa M_\kappa / 18.016 \qquad (10.5.1)$$

and are shown in Fig. 10.5.6. Here, upper-case X denotes mass fraction, lower-case x denotes mole fraction. M_κ is the molecular weight of component κ. For dilute aqueous solutions, the sum appearing in the denominator may be approximated by just retaining the water contribution.

In the third part of the simulation, the benzene/toluene mixture is mobilized by a steamflood. The input file as shown (in part) in Fig. 10.5.7 includes INCON data generated from the waterflood. Steam injection specifications are the same as in *rtcem3*. Fig. 10.5.8 shows part of the printout from this run, including volume and mass balances at initialization, and one-line printouts for the first few time steps. Temperatures near the steam injection point (block AA 1) are rising rapidly, and time steps get reduced due to the severe non-linearities as a gas phase evolves. After the phase change time steps grow again, until a gas phase evolves in the next downstream block. This cyclic behavior continues as the steam front progresses. After 5,000 s of steam injection, the NAPL bank is located in grid blocks AA 39 to AA 42 (INDEX = 6, corresponding to two-phase water-NAPL conditions), similar to the results of the *rtcem3* problem. Upstream from the NAPL bank we have INDEX = 4 (gas-water), downstream we have INDEX = 2 (single-phase water). Benzene is depleted in the NAPL plume relative to toluene, especially in the upstream end, because it is more soluble and more volatile. The final simulation time of 9,000 s is reached after K = 1381 time steps. At this time all VOCs have been completely removed from the system. Results for pressures, temperatures, and phase saturations are very similar to problem *rtce3*.

Fig. 10.5.9 shows the internal version identification messages, as written during program execution to a special disk file VERS, which is copied to the output file at the end of a TMVOC run. Each program unit writes a message when it is called the first time, so that the order in which the messages appear in Fig. 10.5.9 reflects the calling sequence during execution.

```
*rbt1  INJECTION OF TOLUENE AND BENZENE INTO A COLUMN
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
DIRT1    1     2650.      .385   1.6E-11   1.6E-11   1.6E-11       3.1     1000.
     0.e-8        0.      2.85       0.0

CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
toluene
     591.8      41.0     0.263     0.263       0.4
     383.8  -7.28607   1.38091  -2.83433  -2.79168
    92.141-.2435E+020.5125E+00-.2765E-030.4911E-07
      867.    293.00 0.880E-05    303.10      1.41
-.5878E+010.1287E+040.4575E-02-.4499E-05     316.0
 0.101E-03 0.000E+00 0.000E+00 0.000E+00
       0.        0.        0.
benzene
     562.2      48.2     0.271     0.212       0.0
     353.2  -6.98273   1.33213  -2.62863  -3.33399
    78.114-.3392E+020.4739E+00-.3017E-030.7130E-07
      885.    289.00 0.770E-05    273.10      1.52
0.4612E+010.1489E+03-.2544E-010.2222E-04     259.0
 0.411E-03 0.000E+00 0.000E+00 0.000E+00
       0.        0.        0.
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
AIR
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1    1

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    4    4    3    6
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   4  20      2010003000000000 4 0001000
             120.00        2.      120.             9.8060
     1.E-5     1.E02                              1.000E-8               1.e4
    2
            1.013e5                 0.0                 0.0                0.0
               22.0
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .150       .05       .01        3.
    8          0.000      1.84       10.       11.
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1   49    1DIRT1 3.7179E-5

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1AA  2   48    1    1    1     .0091     .0091 2.0428E-3       0.0

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1end 1                         DELV 3.5917E-12 1.0140E+5
AA 50end 2                         DELV 3.5917E-12 1.0140E+5
AA 15tol 1                         COM3   6.488e-5
AA 15ben 2                         COM4   6.592e-5

INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.5.1. TMVOC input file for part 1 of problem 5 (injection of benzene and toluene into a laboratory column).

```
...ITERATING...  AT [   1,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .453951E+00  AT ELEMENT AA 15  EQUATION   4
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 15*  $$$   xsumoil=   .22766E+02
...ITERATING...  AT [   1,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .487433E+03  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   1,  3] --- DELTEX =  .200000E+01   MAX. RES. =  .378773E+00  AT ELEMENT AA 15  EQUATION   3
...ITERATING...  AT [   1,  4] --- DELTEX =  .200000E+01   MAX. RES. =  .792066E-01  AT ELEMENT AA 15  EQUATION   4
...ITERATING...  AT [   1,  5] --- DELTEX =  .200000E+01   MAX. RES. =  .626606E-03  AT ELEMENT AA 15  EQUATION   4
AA 15(   1,  6) ST =  .200000E+01 DT =  .200000E+01 DX1=  .109079E+04 DX2=  .474520E+00 T =  22.000 P =   102391. S =  .000000E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .452984E+00  AT ELEMENT AA 15  EQUATION   4
...ITERATING...  AT [   2,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .184329E-01  AT ELEMENT AA 15  EQUATION   4
...ITERATING...  AT [   2,  3] --- DELTEX =  .200000E+01   MAX. RES. =  .310028E-04  AT ELEMENT AA 15  EQUATION   4
AA 15(   2,  4) ST =  .400000E+01 DT =  .200000E+01 DX1=  .852798E+02 DX2= -.992515E-02 T =  22.000 P =   102476. S =  .000000E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+01   MAX. RES. =  .905938E+00  AT ELEMENT AA 15  EQUATION   4
...ITERATING...  AT [   3,  2] --- DELTEX =  .400000E+01   MAX. RES. =  .262379E-01  AT ELEMENT AA 15  EQUATION   4
...ITERATING...  AT [   3,  3] --- DELTEX =  .400000E+01   MAX. RES. =  .977450E-04  AT ELEMENT AA 15  EQUATION   4
AA 15(   3,  4) ST =  .800000E+01 DT =  .400000E+01 DX1=  .139391E+03 DX2= -.494279E-02 T =  22.000 P =   102615. S =  .000000E+00
...ITERATING...  AT [   4,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .996059E+00  AT ELEMENT AA 15  EQUATION   4
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 14*  $$$   xsumoil=   .18998E+01
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 16*  $$$   xsumoil=   .17279E+01
...ITERATING...  AT [   4,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .785098E-01  AT ELEMENT AA 14  EQUATION   4
...ITERATING...  AT [   4,  3] --- DELTEX =  .800000E+01   MAX. RES. =  .791996E-01  AT ELEMENT AA 14  EQUATION   1
...ITERATING...  AT [   4,  4] --- DELTEX =  .800000E+01   MAX. RES. =  .247685E-02  AT ELEMENT AA 14  EQUATION   4
AA 16(   4,  5) ST =  .160000E+02 DT =  .800000E+01 DX1=  .599063E+02 DX2=  .572931E+00 T =  22.000 P =   102267. S =  .000000E+00
...ITERATING...  AT [   5,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .480126E+00  AT ELEMENT AA 15  EQUATION   4
...ITERATING...  AT [   5,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .123396E+00  AT ELEMENT AA 14  EQUATION   3
...ITERATING...  AT [   5,  3] --- DELTEX =  .800000E+01   MAX. RES. =  .180628E-01  AT ELEMENT AA 16  EQUATION   4
...ITERATING...  AT [   5,  4] --- DELTEX =  .800000E+01   MAX. RES. =  .363176E-04  AT ELEMENT AA 16  EQUATION   4
AA 14(   5,  5) ST =  .240000E+02 DT =  .800000E+01 DX1=  .764895E+02 DX2= -.752827E-01 T =  22.000 P =   102288. S =  .000000E+00
...ITERATING...  AT [   6,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .281065E+00  AT ELEMENT AA 15  EQUATION   4
...ITERATING...  AT [   6,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .603239E-01  AT ELEMENT AA 14  EQUATION   3
...ITERATING...  AT [   6,  3] --- DELTEX =  .800000E+01   MAX. RES. =  .124017E-02  AT ELEMENT AA 14  EQUATION   4
AA 16(   6,  4) ST =  .320000E+02 DT =  .800000E+01 DX1=  .982460E+02 DX2= -.176610E-01 T =  22.000 P =   102454. S =  .000000E+00
...ITERATING...  AT [   7,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .874979E+00  AT ELEMENT AA 14  EQUATION   4
...ITERATING...  AT [   7,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .124924E+00  AT ELEMENT AA 16  EQUATION   1
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 13*  $$$   xsumoil=   .14061E+01
...ITERATING...  AT [   7,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .109257E-01  AT ELEMENT AA 13  EQUATION   4
...ITERATING...  AT [   7,  4] --- DELTEX =  .160000E+02   MAX. RES. =  .501325E-01  AT ELEMENT AA 13  EQUATION   1
...ITERATING...  AT [   7,  5] --- DELTEX =  .160000E+02   MAX. RES. =  .365922E-04  AT ELEMENT AA 12  EQUATION   4
AA 13(   7,  6) ST =  .480000E+02 DT =  .160000E+02 DX1=  .813775E+01 DX2=  .662241E+00 T =  22.000 P =   102100. S =  .000000E+00
...ITERATING...  AT [   8,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .636306E+00  AT ELEMENT AA 14  EQUATION   3
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 17*  $$$   xsumoil=   .36131E+01
...ITERATING...  AT [   8,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .204858E+00  AT ELEMENT AA 13  EQUATION   1
...ITERATING...  AT [   8,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .211662E+00  AT ELEMENT AA 17  EQUATION   1
...ITERATING...  AT [   8,  4] --- DELTEX =  .160000E+02   MAX. RES. =  .154221E-02  AT ELEMENT AA 18  EQUATION   4
AA 17(   8,  5) ST =  .640000E+02 DT =  .160000E+02 DX1=  .789883E+02 DX2=  .526525E+00 T =  22.000 P =   102314. S =  .000000E+00
...ITERATING...  AT [   9,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .410718E+00  AT ELEMENT AA 16  EQUATION   4
...ITERATING...  AT [   9,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .124558E+00  AT ELEMENT AA 13  EQUATION   3
...ITERATING...  AT [   9,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .108176E-01  AT ELEMENT AA 17  EQUATION   4
...ITERATING...  AT [   9,  4] --- DELTEX =  .160000E+02   MAX. RES. =  .135142E-04  AT ELEMENT AA 17  EQUATION   4
AA 18(   9,  5) ST =  .800000E+02 DT =  .160000E+02 DX1=  .132395E+02 DX2=  .215799E-05 T =  22.000 P =   102233. S =  .000000E+00
...ITERATING...  AT [  10,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .413528E+00  AT ELEMENT AA 13  EQUATION   4
...ITERATING...  AT [  10,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .679688E-01  AT ELEMENT AA 13  EQUATION   3
...ITERATING...  AT [  10,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .118587E-02  AT ELEMENT AA 17  EQUATION   4
AA 13(  10,  4) ST =  .960000E+02 DT =  .160000E+02 DX1=  .123046E+03 DX2= -.695716E-02 T =  22.000 P =   102397. S =  .000000E+00
...ITERATING...  AT [  11,  1] --- DELTEX =  .240000E+02   MAX. RES. =  .832972E+00  AT ELEMENT AA 13  EQUATION   3
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 12*  $$$   xsumoil=   .23465E+01
...ITERATING...  AT [  11,  2] --- DELTEX =  .240000E+02   MAX. RES. =  .133132E+00  AT ELEMENT AA 12  EQUATION   4
$$$ 2 ---> 6 $$$ NAPL EVOLVES AT ELEMENT *AA 18*  $$$   xsumoil=   .21059E+01
...ITERATING...  AT [  11,  3] --- DELTEX =  .240000E+02   MAX. RES. =  .342379E+00  AT ELEMENT AA 12  EQUATION   1
...ITERATING...  AT [  11,  4] --- DELTEX =  .240000E+02   MAX. RES. =  .144543E+00  AT ELEMENT AA 18  EQUATION   1
...ITERATING...  AT [  11,  5] --- DELTEX =  .240000E+02   MAX. RES. =  .254532E-02  AT ELEMENT AA 19  EQUATION   4
...ITERATING...  AT [  11,  6] --- DELTEX =  .240000E+02   MAX. RES. =  .132643E-03  AT ELEMENT AA 18  EQUATION   1
AA 18(  11,  7) ST =  .120000E+03 DT =  .240000E+02 DX1=  .475459E+02 DX2=  .618762E+00 T =  22.000 P =   102294. S =  .000000E+00
...
ELEM.  INDEX     P          T          SG          SW          SO          PCwg        PCog        XVOCw        Dgas        DNAPL
                (Pa)      (Deg-C)                                          (Pa)        (Pa)    (mass fract.)  (kg/m**3)   (kg/m**3)

AA  1    1  .10143E+06  .22000E+02  .00000E+00  .10000E+01  .00000E+00  .00000E+00  .00000E+00  .72917E-11  .50594E-03  .87015E+03
AA  2    2  .10148E+06  .22000E+02  .00000E+00  .10000E+01  .00000E+00  .00000E+00  .00000E+00  .47105E-10  .50567E-03  .87017E+03
...
AA 11   11  .10196E+06  .22000E+02  .00000E+00  .10000E+01  .00000E+00  .00000E+00  .00000E+00  .26414E-03  .30729E-02  .87080E+03
AA 12   12  .10208E+06  .22000E+02  .00000E+00  .99555E+00  .44463E-02 -.71165E+02  .00000E+00  .11381E-02  .00000E+00  .87127E+03
AA 13   13  .10261E+06  .22000E+02  .00000E+00  .86785E+00  .13215E+00 -.51340E+03  .00000E+00  .12001E-02  .00000E+00  .87195E+03
AA 14   14  .10322E+06  .22000E+02  .00000E+00  .68822E+00  .31178E+00 -.10114E+04  .00000E+00  .12035E-02  .00000E+00  .87199E+03
AA 15   15  .10366E+06  .22000E+02  .00000E+00  .59132E+00  .40868E+00 -.13518E+04  .00000E+00  .12048E-02  .00000E+00  .87200E+03
AA 16   16  .10329E+06  .22000E+02  .00000E+00  .70690E+00  .29310E+00 -.95396E+03  .00000E+00  .12033E-02  .00000E+00  .87199E+03
AA 17   17  .10273E+06  .22000E+02  .00000E+00  .90125E+00  .98754E-01 -.42373E+03  .00000E+00  .11983E-02  .00000E+00  .87193E+03
AA 18   18  .10229E+06  .22000E+02  .00000E+00  .99915E+00  .84933E-03 -.27289E+02  .00000E+00  .99770E-03  .00000E+00  .86977E+03
AA 19   19  .10224E+06  .22000E+02  .00000E+00  .10000E+01  .00000E+00  .00000E+00  .00000E+00  .99556E-04  .12739E-02  .86989E+03
...
```

Figure 10.5.2. Portion of printout of part 1 of problem 5.

```
*rbt2  WATERFLOOD FOLLOWING INJECTION OF BENZENE AND TOLUENE INTO A COLUMN
...
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   2 100     100100000 00 0202 4 00 1 00
           108.971e3        2.     8000.              9.8060
     1.E-5     1.E02                                1.000e-8                1.e4
    2
             1.013e5                 0.0                 0.0                 0.0
                22.0
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .150       .05       .01        3.
    8          0.000      1.84       10.       11.
...
GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA 50PRO 1                        DELV 3.5917E-12 1.0140E+5
AA  1INJ 1                   3    COM1h
            0.      18.162e3     108.971e3
     3.5382E-4     9.4352e-6     9.4352e-6
      9.2332E4      9.2332E4      9.2332E4

TIMES----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    4
  2.4216e3 15.3368e3  18.162e3 108.971e3
FOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA 50

COFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA 49AA 50

INCON -- INITIAL CONDITIONS FOR   50 ELEMENTS AT TIME   .120000E+03
...
AA 11            .38500000E+00 2
  .1019581644678E+06  .1319033032434E-04  .4537411426046E-04  .2857286371463E-15
  .2200000000000E+02
AA 12            .38500000E+00 6
  .1020833308484E+06  .5076101332413E+00  .4921059092740E+00  .9955537133006E+00
  .2200000000000E+02
AA 13            .38500000E+00 6
  .1026111382101E+06  .4585286594948E+00  .5411873830205E+00  .8678547664117E+00
  .2200000000000E+02
AA 14            .38500000E+00 6
  .1032223263813E+06  .4558709461159E+00  .5438450963995E+00  .6882181111558E+00
  .2200000000000E+02
AA 15            .38500000E+00 6
  .1036608206603E+06  .4548634496830E+00  .5448525928324E+00  .5913245703090E+00
  .2200000000000E+02
AA 16            .38500000E+00 6
  .1032875276398E+06  .4560593766307E+00  .5436566658847E+00  .7068959245514E+00
  .2200000000000E+02
...
ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.5.3. TMVOC input file for part 2 of problem 5 (waterflood).

```
********** VOLUME- AND MASS-BALANCES **********************************************************************************************

********** [KCYC,ITER] = [   0,  0] *****                                  THE TIME IS   .00000E+00 SECONDS, OR   .00000E+00 DAYS

PHASES                      GAS            AQUEOUS           NAPL            TOTAL

VOLUMES     (m**3)     .00000000E+00     .69782561E-03     .17889385E-04     .71571500E-03
MASS       (moles)     .00000000E+00     .38646392E+02     .18456471E+00     .38830957E+02
ENERGY         (J)     .00000000E+00     .64205541E+05     .54076685E+03     .13139982E+06

                        COMPONENTS MOLES IN PLACE - BY PHASES                              COMPONENTS IN PLACE - OVERALL

COMPONENTS              GAS PHASE       AQUEOUS PHASE          NAPL            ADSORBED         TOTAL MOLES     TOTAL MASS (kg)
WATER                  .00000000E+00     .38645141E+02     .52408532E-04                      .38645193E+02     .69623180E+00
AIR                    .00000000E+00     .92996539E-13     .12600223E-14                      .94256562E-13     .27296700E-14
toluene                .00000000E+00     .24601345E-03     .84250577E-01     .00000000E+00     .84496590E-01     .77856003E-02
benzene                .00000000E+00     .10056445E-02     .10026173E+00     .00000000E+00     .10126737E+00     .79103996E-02
total VOCs             .00000000E+00     .12516579E-02     .18451231E+00     .00000000E+00     .18576396E+00     .15696000E-01

**********************************************************************************************************************************


 ...ITERATING...  AT [   1,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .635044E-01  AT ELEMENT AA  1  EQUATION   1
 ...ITERATING...  AT [   1,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .814291E-01  AT ELEMENT AA 15  EQUATION   1
 ...ITERATING...  AT [   1,  3] --- DELTEX =  .200000E+01   MAX. RES. =  .116900E-01  AT ELEMENT AA 13  EQUATION   3
 ...ITERATING...  AT [   1,  4] --- DELTEX =  .200000E+01   MAX. RES. =  .104307E-04  AT ELEMENT AA 14  EQUATION   3
 AA 13(   1,  5) ST =  .200000E+01 DT =  .200000E+01 DX1=  .795020E+04 DX2= -.612368E-05 T =  22.000 P =   110561. S =  .000000E+00
 ...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .926141E-01  AT ELEMENT AA 17  EQUATION   4
 ...ITERATING...  AT [   2,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .609961E-03  AT ELEMENT AA 18  EQUATION   3
 AA 18(   2,  3) ST =  .400000E+01 DT =  .200000E+01 DX1=  .200106E+02 DX2= -.224242E-01 T =  22.000 P =   107570. S =  .000000E+00
 ...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+01   MAX. RES. =  .178082E+00  AT ELEMENT AA 17  EQUATION   4
 ...ITERATING...  AT [   3,  2] --- DELTEX =  .400000E+01   MAX. RES. =  .509336E-02  AT ELEMENT AA 18  EQUATION   3
 ...ITERATING...  AT [   3,  3] --- DELTEX =  .400000E+01   MAX. RES. =  .945002E-04  AT ELEMENT AA 18  EQUATION   4
 AA 18(   3,  4) ST =  .800000E+01 DT =  .400000E+01 DX1=  .194632E+02 DX2= -.418838E-01 T =  22.000 P =   107589. S =  .000000E+00
 ...ITERATING...  AT [   4,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .297803E+00  AT ELEMENT AA 17  EQUATION   4
 ...ITERATING...  AT [   4,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .340290E-01  AT ELEMENT AA 18  EQUATION   3
 ...ITERATING...  AT [   4,  3] --- DELTEX =  .800000E+01   MAX. RES. =  .190926E-02  AT ELEMENT AA 18  EQUATION   4
 AA 19(   4,  4) ST =  .160000E+02 DT =  .800000E+01 DX1= -.499346E-01 DX2=  .568089E-05 T =  22.000 P =   107341. S =  .000000E+00
 ...ITERATING...  AT [   5,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .386451E+00  AT ELEMENT AA 17  EQUATION   4
 ...ITERATING...  AT [   5,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .101071E+00  AT ELEMENT AA 18  EQUATION   1
 ...ITERATING...  AT [   5,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .376500E-02  AT ELEMENT AA 18  EQUATION   4
 AA 18(   5,  4) ST =  .320000E+02 DT =  .160000E+02 DX1=  .131292E+03 DX2= -.205465E-01 T =  22.000 P =   107776. S =  .000000E+00
 ...ITERATING...  AT [   6,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .104407E+01  AT ELEMENT AA 18  EQUATION   4
 ...ITERATING...  AT [   6,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .152958E+00  AT ELEMENT AA 18  EQUATION   1
 ...ITERATING...  AT [   6,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .687798E-01  AT ELEMENT AA 19  EQUATION   4
 ...ITERATING...  AT [   6,  4] --- DELTEX =  .320000E+02   MAX. RES. =  .309425E+00  AT ELEMENT AA 19  EQUATION   1
 ...ITERATING...  AT [   6,  5] --- DELTEX =  .320000E+02   MAX. RES. =  .271432E-02  AT ELEMENT AA 19  EQUATION   4
 AA 19(   6,  6) ST =  .640000E+02 DT =  .320000E+02 DX1=  .467677E+02 DX2=  .509759E+00 T =  22.000 P =   107388. S =  .000000E+00
 ...ITERATING...  AT [   7,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .616791E+00  AT ELEMENT AA 18  EQUATION   3
 ...ITERATING...  AT [   7,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .187907E+00  AT ELEMENT AA 19  EQUATION   1
 ...ITERATING...  AT [   7,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .955892E-02  AT ELEMENT AA 19  EQUATION   1
 AA 20(   7,  4) ST =  .960000E+02 DT =  .320000E+02 DX1= -.232142E+00 DX2=  .801196E-05 T =  22.000 P =   107152. S =  .000000E+00
...

         *rbt2  WATERFLOOD FOLLOWING INJECTION OF BENZENE AND TOLUENE INTO A COLUMN

                                                                    KCYC =   60  -  ITER =    3  -  TIME =  .10897E+06

                                  >>>>>>>>>> MOLE FRACTIONS IN THE  OIL  PHASE <<<<<<<<<<

 ELEM. INDEX   Xwat      2 AIR       3 toluene   4 benzene  ** SUMmolef
...
 AA 18   2   .28396E-03  .30116E-31  .26211E-01  .23894E-06  .00000E+00
 AA 19   6   .28396E-03  .11102E-15  .99930E+00  .41844E-03  .00000E+00
 AA 20   6   .28396E-03  .00000E+00  .99805E+00  .16693E-02  .00000E+00
 AA 21   6   .28396E-03  .00000E+00  .99489E+00  .48248E-02  .00000E+00
 AA 22   6   .28396E-03  .00000E+00  .98798E+00  .11741E-01  .00000E+00
 AA 23   6   .28396E-03  .11102E-15  .97409E+00  .25622E-01  .00000E+00
 AA 24   6   .28396E-03  .33307E-15  .94856E+00  .51153E-01  .00000E+00
 AA 25   6   .28396E-03  .77716E-15  .90340E+00  .96312E-01  .00000E+00
 AA 26   6   .28396E-03  .15543E-14  .83382E+00  .16590E+00  .00000E+00
 AA 27   6   .28396E-03  .18874E-14  .74773E+00  .25199E+00  .00000E+00
 AA 28   6   .28396E-03  .14433E-14  .66382E+00  .33590E+00  .00000E+00
 AA 29   6   .28396E-03  .77716E-15  .59792E+00  .40180E+00  .00000E+00
 AA 30   6   .28396E-03  .11102E-15  .55385E+00  .44586E+00  .00000E+00
 AA 31   6   .28396E-03  .00000E+00  .52959E+00  .47013E+00  .00000E+00
 AA 32   2   .28396E-03  .10000E-29  .52880E+00  .47091E+00  .00000E+00
```

Figure 10.5.4. Portion of printout of part 2 of problem 5.

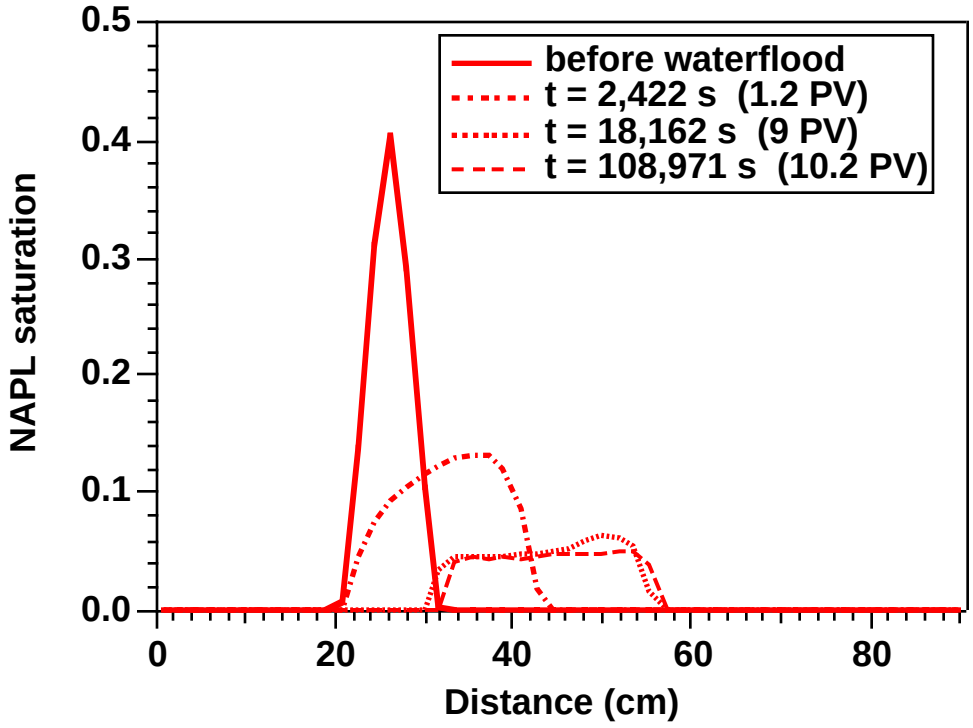


Figure 10.5.5. NAPL bank before waterflood, and after injection of 1.2, 9, and 10.2 pore volumes of water.

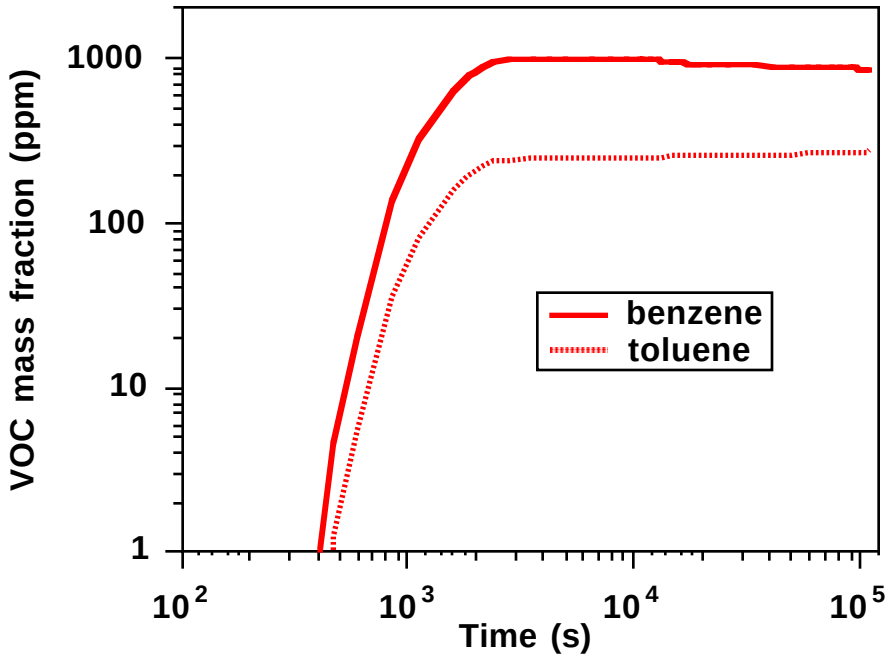


Figure 10.5.6. Benzene and toluene mass fractions at outlet (grid block AA 50) during waterflood.

```
*rbt3* STEAMFLOOD OF BENZENE AND TOLUENE BANK FOLLOWING WATERFLOOD
.....  first VOC is toluene, the less volatile !
...
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    4    5    3    6
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   21999    199910003000000202 4 00 1 00
               9.e3        2.     2000.              9.8060
     1.E-5     1.E02                                1.000e-8               1.e+4
    2
              1.013e5                 0.0                 0.0                 0.0
                22.0
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .150       .05       .01        3.
    8          0.000      1.84       10.       11.
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1   49    1DIRT1 3.7179E-5

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA  1AA  2   48    1    1    1     .0091     .0091 2.0428E-3       0.0

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AA 50PRO 1                        DELV 3.5917E-12 1.0140E+5
AA  1INJ 1                        COM1 3.5341E-05   1.562e6

...
INCON -- INITIAL CONDITIONS FOR   50 ELEMENTS AT TIME   .108971E+06
AA 27            .38500000E+00 6
  .1017932226398E+06  .7477291645795E+00  .2519868779359E+00  .9526954058678E+00
  .2200000000000E+02
AA 28            .38500000E+00 6
  .1017906614922E+06  .6638198479568E+00  .3358961945586E+00  .9516768325772E+00
  .2200000000000E+02
AA 29            .38500000E+00 6
  .1017872427058E+06  .5979170037600E+00  .4017990387553E+00  .9509027701144E+00
  .2200000000000E+02
AA 30            .38500000E+00 6
  .1017815941334E+06  .5538524966174E+00  .4458635458980E+00  .9507931440888E+00
  .2200000000000E+02
AA 31            .38500000E+00 6
  .1017509996762E+06  .5295881068954E+00  .4701279356200E+00  .9580123487215E+00
  .2200000000000E+02
...
ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.5.7. TMVOC input file for part 3 of problem 5 (steamflood).

```
********** VOLUME- AND MASS-BALANCES **********************************************************************************************

********** [KCYC,ITER] = [   0,  0] *****                                    THE TIME IS   .00000E+00 SECONDS, OR   .00000E+00 DAYS

PHASES                      GAS             AQUEOUS           NAPL             TOTAL

VOLUMES     (m**3)     .00000000E+00     .70746304E-03     .82519626E-05     .71571500E-03
MASS       (moles)     .00000000E+00     .39161981E+02     .79968328E-01     .39241950E+02
ENERGY         (J)     .00000000E+00     .65062134E+05     .24924204E+03     .13196489E+06


                        COMPONENTS MOLES IN PLACE - BY PHASES                              COMPONENTS IN PLACE - OVERALL

COMPONENTS              GAS PHASE       AQUEOUS PHASE          NAPL            ADSORBED         TOTAL MOLES     TOTAL MASS (kg)
WATER                  .00000000E+00     .39156711E+02     .22707605E-04                     .39156733E+02     .70544771E+00
AIR                    .00000000E+00     .11026079E-12     .91877281E-15                     .11117956E-12     .32197601E-14
toluene                .00000000E+00     .16175920E-02     .64885834E-01     .00000000E+00     .66503426E-01     .61276922E-02
benzene                .00000000E+00     .36531916E-02     .15059786E-01     .00000000E+00     .18712978E-01     .14617456E-02
total VOCs             .00000000E+00     .52707836E-02     .79945620E-01     .00000000E+00     .85216404E-01     .75894377E-02

************************************************************************************************************************************


...ITERATING...  AT [   1,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .409993E-01  AT ELEMENT AA  1  EQUATION   5
...ITERATING...  AT [   1,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .113095E-03  AT ELEMENT AA  2  EQUATION   5
AA  1(   1,  3) ST =  .200000E+01 DT =  .200000E+01 DX1=  .752822E+03 DX2=  .949664E-21 T =  22.856 P =   102413. S =  .000000E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .400000E+01   MAX. RES. =  .746522E-01  AT ELEMENT AA  1  EQUATION   5
...ITERATING...  AT [   2,  2] --- DELTEX =  .400000E+01   MAX. RES. =  .323629E-04  AT ELEMENT AA  1  EQUATION   5
AA  1(   2,  3) ST =  .600000E+01 DT =  .400000E+01 DX1=  .256845E+01 DX2=  .507170E-21 T =  24.542 P =   102416. S =  .000000E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .136824E+00  AT ELEMENT AA  1  EQUATION   5
...ITERATING...  AT [   3,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .148319E-03  AT ELEMENT AA  1  EQUATION   5
AA  2(   3,  3) ST =  .140000E+02 DT =  .800000E+01 DX1=  .368491E+01 DX2=  .000000E+00 T =  22.229 P =   102401. S =  .000000E+00
...ITERATING...  AT [   4,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .234031E+00  AT ELEMENT AA  1  EQUATION   5
...ITERATING...  AT [   4,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .802509E-03  AT ELEMENT AA  1  EQUATION   1
AA  2(   4,  3) ST =  .300000E+02 DT =  .160000E+02 DX1=  .580288E+01 DX2=  .000000E+00 T =  22.928 P =   102407. S =  .000000E+00
...ITERATING...  AT [   5,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .361042E+00  AT ELEMENT AA  1  EQUATION   5
...ITERATING...  AT [   5,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .407328E-02  AT ELEMENT AA  1  EQUATION   1
AA  2(   5,  3) ST =  .620000E+02 DT =  .320000E+02 DX1=  .750071E+01 DX2=  .000000E+00 T =  25.309 P =   102414. S =  .000000E+00
...ITERATING...  AT [   6,  1] --- DELTEX =  .640000E+02   MAX. RES. =  .488902E+00  AT ELEMENT AA  1  EQUATION   5
...ITERATING...  AT [   6,  2] --- DELTEX =  .640000E+02   MAX. RES. =  .172338E-01  AT ELEMENT AA  2  EQUATION   5
...ITERATING...  AT [   6,  3] --- DELTEX =  .640000E+02   MAX. RES. =  .334563E-04  AT ELEMENT AA  2  EQUATION   5
AA  2(   6,  4) ST =  .126000E+03 DT =  .640000E+02 DX1=  .688735E+01 DX2=  .126565E-21 T =  32.258 P =   102421. S =  .000000E+00
...ITERATING...  AT [   7,  1] --- DELTEX =  .128000E+03   MAX. RES. =  .577735E+00  AT ELEMENT AA  1  EQUATION   5
...ITERATING...  AT [   7,  2] --- DELTEX =  .128000E+03   MAX. RES. =  .532568E-01  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   7,  3] --- DELTEX =  .128000E+03   MAX. RES. =  .165624E-03  AT ELEMENT AA  2  EQUATION   5
AA  2(   7,  4) ST =  .254000E+03 DT =  .128000E+03 DX1=  .241124E+01 DX2=  .264625E-19 T =  48.944 P =   102424. S =  .000000E+00
...ITERATING...  AT [   8,  1] --- DELTEX =  .256000E+03   MAX. RES. =  .677115E+00  AT ELEMENT AA  2  EQUATION   5
$$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AA  1*  $$$   PX =   .10240E+06  PG =   .27826E+06
...ITERATING...  AT [   8,  2] --- DELTEX =  .256000E+03   MAX. RES. =  .336074E+05  AT ELEMENT AA  2  EQUATION   5
+++++++++ excessive residual =  .336074E+05
+++++++++ REDUCE TIME STEP AT (   8,  2) +++++++++++++++++   NEW DELT =  .640000E+02
...ITERATING...  AT [   8,  1] --- DELTEX =  .640000E+02   MAX. RES. =  .169279E+00  AT ELEMENT AA  2  EQUATION   5
$$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AA  1*  $$$   PX =   .10243E+06  PG =   .11928E+06
...ITERATING...  AT [   8,  2] --- DELTEX =  .640000E+02   MAX. RES. =  .514236E+03  AT ELEMENT AA  2  EQUATION   5
...ITERATING...  AT [   8,  3] --- DELTEX =  .640000E+02   MAX. RES. =  .141352E+03  AT ELEMENT AA  2  EQUATION   5
...ITERATING...  AT [   8,  4] --- DELTEX =  .640000E+02   MAX. RES. =  .430666E+02  AT ELEMENT AA  2  EQUATION   5
...ITERATING...  AT [   8,  5] --- DELTEX =  .640000E+02   MAX. RES. =  .548582E+01  AT ELEMENT AA  2  EQUATION   5
...ITERATING...  AT [   8,  6] --- DELTEX =  .640000E+02   MAX. RES. =  .399707E+01  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   8,  7] --- DELTEX =  .640000E+02   MAX. RES. =  .298861E+00  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   8,  8] --- DELTEX =  .640000E+02   MAX. RES. =  .367425E-01  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   8,  9] --- DELTEX =  .640000E+02   MAX. RES. =  .789110E-02  AT ELEMENT AA  1  EQUATION   1
+++++++++ REDUCE TIME STEP AT (   8,  9) +++++++++++++++++   NEW DELT =  .160000E+02
...ITERATING...  AT [   8,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .423197E-01  AT ELEMENT AA  2  EQUATION   5
...ITERATING...  AT [   8,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .758309E-04  AT ELEMENT AA  1  EQUATION   1
AA  1(   8,  3) ST =  .270000E+03 DT =  .160000E+02 DX1=  .917478E+01 DX2=  .800481E-20 T =  95.557 P =   102439. S =  .000000E+00
...ITERATING...  AT [   9,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .824739E-01  AT ELEMENT AA  2  EQUATION   5
$$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AA  1*  $$$   PX =   .10244E+06  PG =   .10874E+06
...ITERATING...  AT [   9,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .911235E+02  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   9,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .193422E+02  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   9,  4] --- DELTEX =  .320000E+02   MAX. RES. =  .388879E+01  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   9,  5] --- DELTEX =  .320000E+02   MAX. RES. =  .178321E+00  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [   9,  6] --- DELTEX =  .320000E+02   MAX. RES. =  .109658E-01  AT ELEMENT AA  2  EQUATION   5
...ITERATING...  AT [   9,  7] --- DELTEX =  .320000E+02   MAX. RES. =  .197991E-03  AT ELEMENT AA  1  EQUATION   1
AA  2(   9,  8) ST =  .302000E+03 DT =  .320000E+02 DX1=  .244305E+04 DX2=  .749299E-19 T =  59.850 P =   104876. S =  .000000E+00
...ITERATING...  AT [  10,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .274506E+00  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [  10,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .653083E+01  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [  10,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .212738E+01  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [  10,  4] --- DELTEX =  .320000E+02   MAX. RES. =  .246199E+00  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [  10,  5] --- DELTEX =  .320000E+02   MAX. RES. =  .198338E-01  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [  10,  6] --- DELTEX =  .320000E+02   MAX. RES. =  .643752E-03  AT ELEMENT AA  1  EQUATION   1
AA  2(  10,  7) ST =  .334000E+03 DT =  .320000E+02 DX1= -.907045E+03 DX2= -.567399E-19 T =  71.044 P =   103969. S =  .000000E+00
...ITERATING...  AT [  11,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .206957E+00  AT ELEMENT AA  1  EQUATION   1
...ITERATING...  AT [  11,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .395476E-01  AT ELEMENT AA  2  EQUATION   1
...ITERATING...  AT [  11,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .188018E-03  AT ELEMENT AA  3  EQUATION   5
AA  1(  11,  4) ST =  .366000E+03 DT =  .320000E+02 DX1= -.133458E+04 DX2= -.152841E-19 T = 100.992 P =   104967. S =  .361338E+00
```

Figure 10.5.8. Portion of printout for part 3 of problem 5 (steamflood).

```
 *rbt3* STEAMFLOOD OF BENZENE AND TOLUENE BANK FOLLOWING WATERFLOOD

          OUTPUT DATA AFTER (  690,  3)-2-TIME STEPS                                                    THE TIME IS   .57870E-01 DAYS
@@@
```

```
*****************************************************************************************************************************
*                                                                                                                           *
*                                                SUMMARY OF PROGRAM UNITS USED                                              *
*                                                                                                                           *
*****************************************************************************************************************************

      UNIT    VERSION     DATE                COMMENTS
-----------------------------------------------------------------------------------------------------------------------------

     IO       1.0      15 APRIL     1991      OPEN FILES *VERS*, *MESH*, *INCON*, *GENER*, *SAVE*, *LINEQ*, AND *TABLE*
     SECOND   1.0       6 September 1994      CPU timing function for IBM RS/6000

     TOUGH2   2.00      5 September 2001      MAIN PROGRAM
                                              special version for conjugate gradient package T2CG2
                                              includes definition of coordinate arrays and radiative heat transfer capability
                                              has additional COMMON blocks for TMVOC

     INPUT    2.0       4 January   2002      READ ALL DATA PROVIDED THROUGH FILE *INPUT*
     FLOP     1.0      11 APRIL     1991      CALCULATE NUMBER OF SIGNIFICANT DIGITS FOR FLOATING POINT ARITHMETIC

     RFILE    1.5      24 April     2001      INITIALIZE DATA FROM FILES *MESH* OR *MINC*, *GENER*, AND *INCON*
                                              also initializes permeability modifiers and coordinate arrays
                                              and optionally reads tables with flowing wellbore pressures
     PMIN     1.0      26 September 1997      initialize block-by-block permeability modifiers
     SINSUB   1.00      1 October   1999      initialize parameters for the solver package, and generate informative printout

     CYCIT    1.01     20 September 2001      EXECUTIVE ROUTINE FOR MARCHING IN TIME

     EOS      2.00      3 January   2002      *EMVOC* FLUID PROPERTY MODULE FOR WATER/multiple NCGs/multiple VOCs
                                              includes multiphase diffusion
     SATO     1.00     21 November  2000      CALCULATE HYDROCARBON VAPOR PRESSURE FROM EITHER
                                               WAGNER OR ANTOINE EQUATIONS.
     SRKZ     1.00      9 August    2001      calculate molar volume and departure enthalpy of a gas mixture
                                               from the Soave-Redlich-Kwong or Peng-Robinson EOS
     CUBROOT  1.00     25 December  2000      solve general cubic equation
     HOFVAP   1.00     30 October   2000      enthalpy of vaporization for hydrocarbons
     SAT      1.0 S    17 SEPTEMBER 1990      STEAM TABLE EQUATION: SATURATION PRESSURE AS FUNCTION OF TEMPERATURE (M. OS.)
     solwat   1.0      30 November  2000      Solubility of water in NAPL as a function of T
     SOLUB    1.00     30 October   2000      CALCULATES AQUEOUS PHASE SOLUBILITIES OF HYDROCARBON COMPONENTS
     HCO      1.00      6 August    1997      CALCULATES HENRYs CONSTANTS FOR HYDROCARBON COMPONENTS
     HENRY    1.0      15 January   2002      Calculates Henrys constant for NCGs as a function of  temperature.
     COWAT    1.0 S    17 SEPTEMBER 1990      LIQUID WATER DENSITY AND INT. ENERGY VERSUS TEMPERATURE AND PRESSURE (M. OS.)
     VISH2O   1.0      15 September 2000      VISCOSITY OF LIQ. WATER OR VAPOR vs. TEMPERATURE AND DENSITY (ASME, 1977)
     PCAP     1.1  !   21 June      2001      CAPILLARY PRESSURE AS FUNCTION OF SATURATION (INCL 3-PHASE)
                                              for ICP=10 use Parkers ICP=8 with fixes
     COWATO1  1.00     23 August    2001      MOLAR VOLUME AND ENTHALPY OF LIQUID HYDROCARBON MIXTURE
     SRK      1.00      9 August    2001      SRK or PR EQUATION OF STATE FOR GAS MIXTURES
     RELP     1.11     25 June      2001      RELATIVE PERMEABILITIES AS FUNCTIONS OF SATURATION (INCL 3-PHASE)
                                               for IRP = 6 ("STONE I"), take Swr = min(Swr,Sw) for calculating krn
     SRK1     1.00      9 August    2001      calculate the departure enthalpy of hydrocarbon components in the
                                               oil phase from the SRK or PR equation of state
     IDEAL1   1.00     21 November  2000      IDEAL GAS MOLAR ENTHALPY OF A GAS MIXTURE IN
     VISOILL  1.01     21 November  2000      VISCOSITY OF A LIQUID MIXTURE OF HYDROCARBONS

     BALLA    2.00     28 August    2001      PERFORM SUMMARY BALANCES FOR VOLUME, MASS, AND ENERGY
     TSTEP    1.0       4 MARCH     1991      ADJUST TIME STEPS TO COINCIDE WITH USER-DEFINED TARGET TIMES

     MULTI    2.0      30 August    2001      ASSEMBLE ALL ACCUMULATION AND FLOW TERMS
                                              includes capabilities for radiative heat transfer and diffusion in all phases
                                                 with local equilibrium phase partitioning between gas and liquid
                                              allows block-by-block permeability modification
                                              permeability changes from precip. (EWASG) through PAR(NLOC2S+3)
                                              TMVOC-compatible version


     QU       2.0      30 August    2001      ASSEMBLE ALL SOURCE AND SINK TERMS
                                              "rigorous" step rate capability for MOP(12) = 2,
                                              and capability for flowing wellbore pressure corrections
     PHASD    1.0      14 November  2001      calculate composition, rate and enthalpy for wells on deliverability
     AMOLW    2.0      23 August    2001      calculate molecular weight of phase mixtures
     WMASSD   2.00     23 August    2001      convert molar densities to mass densities
     LINEQ    2.00      4 October   1999      Interface for linear equation solvers T2CG2
                                              Can call a direct solver or a package of conjugate gradient solvers
     MTRXIN   1.1      10 September 2000      Routine for Z-preprocessing of the Jacobian

     CONVER   1.0      19 April     2000      UPDATE PRIMARY VARIABLES AFTER CONVERGENCE IS ACHIEVED
     FGTAB    1.00     14 January   2002      Tabulate element, connection, and generation data vs. time for plotting
     SUPST    1.0 S     1 February  1991      VAPOR DENSITY AND INTERNAL ENERGY AS FUNCTION OF TEMPERATURE AND PRESSURE (M. OS.)
     IDEAL    1.00     25 June      2001      IDEAL GAS MOLAR ENTHALPY OF GAS MIXTURE MINUS H2O
     VISGAS   2.00     21 August    2001      MAIN SUBROUTINE FOR THE VISCOSITY OF THE GAS PHASE
     VISNCG   2.0      20 November  2001      VISCOSITY OF NCG AS FUNCTION OF TEMPERATURE
     VISCOHC  1.00     22 November  2000      gas viscosities of pure hydrocarbon components
     GASNAPL  2.00     21 August    2001      flash calculation for evolving a NAPL phase
     RTSAFE   1.00     27 June      2001      PART OF NEWTON-RAPHSON ALGORITHM FOR FLASH CALCULATION
     FUNCD    2.00     21 August    2001      ancillary routine for RTSAFE

     OUT      2.00     21 December  2001      PRINT RESULTS FOR ELEMENTS, CONNECTIONS, AND SINKS/SOURCES
     WRIFI    1.0      12 April     2001      AT THE COMPLETION OF A TOUGH2 RUN, WRITE PRIMARY VARIABLES ON FILE *SAVE*

*****************************************************************************************************************************
```

Figure 10.5.9. Calling sequence of program units in part 3 of problem 5.

10.6 Problem No. 6 (*rad*) – Air Displacement of a NAPL from a Laboratory Column

This problem is an adaptation of the numerical simulation of a laboratory experiment presented by Ho (1995), who used the original M2NOTS code. The flow system is a sand column 18 cm high with a cross sectional area of 3.4×10^{-4} m^2. The mesh has 18 evenly spaced elements with a spacing of 1 cm; two additional elements, placed on top and bottom of the column, are used to set different boundary conditions. The simulation consists of four parts that involve (1) obtaining a gas-static equilibrium as initial state, (2) injection of a NAPL consisting of a mixture of xylene and toluene, (3) redistribution of NAPL under gravity and capillary forces, and (4) removal of NAPL by airflooding. All simulations are run in isothermal mode, with NEQ = NK specified in data block MULTI.

The first part of the simulation obtains a gas-static equilibrium by specifying constant conditions of $P = 1.01 \times 10^5$ Pa and T = 20 °C for inactive element AJ 1 at the bottom of the column (input file *rad1*; Fig. 10.6.1). Initially, the column contains gas phase only with no VOC present. Gas composition is specified as mole fractions of 20.79 % for oxygen and 78.21 % for nitrogen; the remaining 1% mole fraction corresponds to water vapor. We set NK= 3 in data block MULTI to initialize the system with three-component (water, oxygen, nitrogen) initial conditions, and NEQ = 3 to specify a constant temperature simulation. The pressure-equilibrated conditions obtained are introduced as data block INCON in the input file for the second part of the simulation, Fig. 10.6.2.

The second part of the simulation involves the injection of a liquid mixture of o-xylene (component #4) and toluene (component #5) into the top of the column (grid block A11 1). We set NK = 5 in data block MULTI for this 5-component run, and assign NKIN = 3 to be able to initialize from the VOC-free 3-component initial conditions obtained in the first run segment. Constant boundary conditions are used at both ends of the column, by specifying numerically infinite volumes for the two boundary elements in block ELEME. The NAPL mixture is injected at a constant total rate of 1 ml/min for 216 s, to inject a total volume of 3.6 ml of NAPL. The injected rate is shared between o-xylene and toluene by chosing the COM3 and COM4 options for TYPE in record GENER.1. The various constants used to compute the thermophysical properties of o-xylene and toluene are contained in data block CHEMP, where this time NHC = 2 is assigned. Details of the Stone I three-phase relative permeability functions (IRP = 6 in record RPCAP.1) and Parker's three-phase capillary pressure functions (ICP = 8 in record RPCAP.2) may be found in Appendices G and H, respectively. Molecular diffusion is included for all components in all phases. The desired simulation time of 216 s is reached after 43 time steps. Some of the printed output is shown in Fig. 10.6.3.

The third part of the simulation models redistribution of the injected NAPL under gravity and capillary forces over a two-day period, with both sides of the column closed. These boundary conditions were realized by simply changing the name of the two boundary elements in block CONNE, so that the two connections across the boundary involve unknown elements and will be ignored by TMVOC (Fig. 10.6.4). The initial conditions for this part of the simulation are the conditions at the end of the second part of the simulation. Block GENER has been removed to stop the injection of NAPL. Data block SOLVR was introduced to select matrix solver # 5 with Z1-preconditioning. The SAVE file generated by the second part of the simulation was placed into the input file, shown (partly) in Figure 10.6.4. A partial printout of results is given in Figure 10.6.5. It is seen that the NAPL has drained towards the bottom of the column. Composition of NAPL and gas phases is rather uniform throughout.

The fourth and final part of the simulation consists of air injection into the bottom of the column for a time period of 7200 s (120 minutes). The input file is shown (partly) in Figure 10.6.6. Again, the initial conditions for this part of the problem are the conditions at the end of the previous simulation. GENER data specify injection of oxygen and nitrogen at a total rate of 1.2×10^{-5} kg/s and in proportions that correspond to mole fractions of 21 % and 79 %, respectively. Printout is specified at intermediate times of 15, 29, 45 and 100 minutes after start of air injection using data block TIMES. We also include an FOFT data block for generating time series for element A11 1 at the top of the column. A revised version of subroutine FGTAB was used, in which the first 5 primary variables are written out (see sec. 10.5). A large specific heat is used in domain ATMO2, so that the large-volume grid block representing the top boundary condition will be excluded from the summary of volume and mass balances.

Part of the output after 2,700 s of air injection is shown in Figure 10.6.7. The NAPL is seen to have been completely vaporized and removed from the two bottommost elements. The more volatile toluene was removed preferentially, so that the remaining NAPL becomes strongly enriched in o-xylene (compare with Fig. 10.6.5). Fig. 10.6.8 shows profiles of o-xylene and toluene concentrations in the NAPL phase after 1,740 s, indicating the preferential removal of toluene at the bottom of the column, and large compositional gradients. After 2,700 s, 98.3 % of the initial toluene inventory is removed, while only 29.3 % of the o-xylene is removed. The evolution of NAPL saturation and gas phase composition at the top of the column is shown in Fig. 10.6.9. Toluene concentration in the gas phase is five times larger than that of o-xylene initially. Concentrations change little up to 2,500 s, when complete removal of toluene is approached. Increasing o-xylene concentration in the NAPL phase increases the vapor pressure and hence the xylene concentration

in gas in the period from 2,000 to 3,500 s. After NAPL disappears from the outlet element o-xylene concentrations decline. At the final simulation time of 7,200 s all VOCs have been removed from the system.

```
*rad1* .. air displacement of a NAPL from a lab. column (prep. of initial state)
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3     2650.      .350   8.4E-11   8.4E-11   8.4E-11       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .100       .08      .000       1.2
    8          0.100      2.00       40.       20.
ATMO2    3       10.      .990   8.4E-11   8.4E-11   8.4E-09       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .600       .05      .000        3.
    9

CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
O2
N2
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    3    3    3    8
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   3  25      2510003000000000 4 0001000                1.8
              21.e12       -1.                      9.8065
        .1        1.       10.      100.     8000.
     1.E-6     1.E01                              1.000E-8               1.e4
    1
               1.0e5              0.2079              0.7821               20.0
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
     2.e-5    6.e-10    6.e-10
     2.e-5    6.e-10    6.e-10
     2.e-5    6.e-10    6.e-10
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .100       .08      .000       1.8
    8          0.000      2.00       40.       20.
GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A   1              2 .3400E-050.3400E-03          0.1700E-010.5000E-02 .0000E-00
A11 1              1 .3400E-050.0000E+00          0.1700E-010.5000E-02-.5000E-02
...
AI1 1             10.3400E-050.3400E-03          0.1700E-010.5000E-02-.1750E+00
AJ  1              2-.3400E+450.3400E-03          0.1700E-010.5000E-02-.1800E+00

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A   1A11 1                   3 .1000E-030.5000E-020.3400E-030.1000E+01
...
INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AJ  1                     0.99 1
              1.01e5              0.2079              0.7821               20.0

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.6.1. TMVOC input file for part 1 of problem 6.

```
*rad2* .. air displacement of a NAPL from a lab. column (injection of NAPL)
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3     2650.      .350   8.4E-11   8.4E-11   8.4E-11       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .100       .08      .000       1.8
    8          0.100      2.00       40.       20.
ATMO2    3       10.      .990   8.4E-11   8.4E-11   8.4E-09       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .600       .05      .000        3.
    9

CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
o-xylene
     630.3      37.3     0.262     0.310       0.5
     417.6  -7.53357   1.40968  -3.10985  -2.85992
   106.168-.1585E+020.5962E+00-.3443E-030.7528E-07
      880.    293.00 0.708E-05    293.00      1.93
                        0.5900   293.000     369.0
 0.322E-04 0.000E+00 0.000E+00 0.000E+00
 0.550E+00     0.000
toluene
     591.8      41.0     0.263     0.263       0.4
     383.8  -7.28607   1.38091  -2.83433  -2.79168
    92.141-.2435E+020.5125E+00-.2765E-030.4911E-07
      867.    293.00 0.880E-05    303.10      1.41
-.5878E+010.1287E+040.4575E-02-.4499E-05     316.0
 0.101E-03 0.000E+00 0.000E+00 0.000E+00
        0.        0.        0.
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
O2
N2
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1

     NKIN=3 allows to read incon data generated by *rad1* with NK=3 !!!
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    5    5    3    8    3
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   3 100      2510003000000000 4 0004000                1.8
               216.0       -1.                      9.8065
    .25e-1
     1.E-5     1.E02                                1.000E-8                1.e4
    1
               1.0e5              0.2079              0.7821                20.0
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
     2.e-5    6.e-10    6.e-10
     2.e-5    6.e-10    6.e-10
     2.e-5    6.e-10    6.e-10
    7.3e-5    6.e-10    6.e-10
    7.9e-5    6.e-10    6.e-10
```

Figure 10.6.2. TMVOC input file for part 2 of problem 6 (NAPL injection).

```
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .100       .08      .000       1.8
    8          0.000      2.00       40.       20.
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
...
CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
...
INCON -- INITIAL CONDITIONS FOR   20 ELEMENTS AT TIME   .332011E+07
A   1            .99000000E+00 1
  .1009978868521E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A11 1            .35000000E+00 1
  .1009979466575E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A21 1            .35000000E+00 1
  .1009980639232E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A31 1            .35000000E+00 1
  .1009981811891E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A41 1            .35000000E+00 1
  .1009982984551E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A51 1            .35000000E+00 1
  .1009984157212E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A61 1            .35000000E+00 1
  .1009985329875E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A71 1            .35000000E+00 1
  .1009986502539E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A81 1            .35000000E+00 1
  .1009987675204E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
A91 1            .35000000E+00 1
  .1009988847871E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AA1 1            .35000000E+00 1
  .1009990020539E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AB1 1            .35000000E+00 1
  .1009991193209E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AC1 1            .35000000E+00 1
  .1009992365880E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AD1 1            .35000000E+00 1
  .1009993538552E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AE1 1            .35000000E+00 1
  .1009994711225E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AF1 1            .35000000E+00 1
  .1009995883900E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AG1 1            .35000000E+00 1
  .1009997056577E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AH1 1            .35000000E+00 1
  .1009998229254E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AI1 1            .35000000E+00 1
  .1009999401933E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02
AJ  1            .99000000E+00 1
  .1010000000000E+06  .2079000000000E+00  .7821000000000E+00  .2000000000000E+02

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A11 1xyl 1                       COM4  7.3578e-6    300.e3
A11 1tol 2                       COM5  7.2012e-6    300.e3

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.6.2. TMVOC input file for part 2 of problem 6 (continued).

```
...ITERATING...  AT [   1,  1] --- DELTEX =  .250000E-01   MAX. RES. =  .574647E-02  AT ELEMENT A11 1  EQUATION   5
$$$ 1 ---> 5 $$$ NAPL EVOLVES AT ELEMENT *A11 1*  $$$   xsumoil=   .65016E+01
...ITERATING...  AT [   1,  2] --- DELTEX =  .250000E-01   MAX. RES. =  .454543E-02  AT ELEMENT A11 1  EQUATION   4
...ITERATING...  AT [   1,  3] --- DELTEX =  .250000E-01   MAX. RES. =  .162590E-03  AT ELEMENT A11 1  EQUATION   5
A11 1(   1,  4) ST =  .250000E-01 DT =  .250000E-01 DX1=  .245090E+01 DX2=  .356221E-02 T =  20.000 P =   101000. S =  .999730E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .500000E-01   MAX. RES. =  .112535E-01  AT ELEMENT A11 1  EQUATION   5
...ITERATING...  AT [   2,  2] --- DELTEX =  .500000E-01   MAX. RES. =  .321205E-02  AT ELEMENT A11 1  EQUATION   5
A11 1(   2,  3) ST =  .750000E-01 DT =  .500000E-01 DX1= -.225637E+01 DX2= -.325484E-03 T =  20.000 P =   100998. S =  .999041E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .100000E+00   MAX. RES. =  .225896E-01  AT ELEMENT A11 1  EQUATION   5
...ITERATING...  AT [   3,  2] --- DELTEX =  .100000E+00   MAX. RES. =  .151966E-02  AT ELEMENT A11 1  EQUATION   5
A11 1(   3,  3) ST =  .175000E+00 DT =  .100000E+00 DX1= -.784692E-01 DX2= -.935554E-04 T =  20.000 P =   100998. S =  .997656E+00
...ITERATING...  AT [   4,  1] --- DELTEX =  .200000E+00   MAX. RES. =  .451823E-01  AT ELEMENT A11 1  EQUATION   5
...ITERATING...  AT [   4,  2] --- DELTEX =  .200000E+00   MAX. RES. =  .112479E-02  AT ELEMENT A11 1  EQUATION   5
A11 1(   4,  3) ST =  .375000E+00 DT =  .200000E+00 DX1= -.126404E-01 DX2= -.374667E-04 T =  20.000 P =   100998. S =  .994883E+00
...

*rad2* .. air displacement of a NAPL from a lab. column (injection of NAPL)

         OUTPUT DATA AFTER (  43,  4)-2-TIME STEPS                                                    THE TIME IS   .25000E-02 DAYS
@@@
```

```
*rad3* .. air displacement of a NAPL from a lab. column (redistribut.)
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3     2650.      .350   8.4E-11   8.4E-11   8.4E-11       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .100       .08      .000       1.8
    8          0.000      2.00       40.       20.
ATMO2    3       10.      .990   8.4E-11   8.4E-11   8.4E-09       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .600       .05      .000        3.
    9


...
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    5    5    3    8
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1

START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   3 100     100100003000000000 4 0004000                1.8
             1728.e2       -1.                        9.8065
     1.e+0
     1.E-5     1.E02                                1.000E-8                1.e4
    1
             1.000e5                0.00                0.0                0.00
                0.99                20.0
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
...

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AZ  1A11 1                   3 .1000E-030.5000E-020.3400E-030.1000E+01
A11 1A21 1                   30.5000E-020.5000E-020.3400E-030.1000E+01
...
AH1 1AI1 1                   30.5000E-020.5000E-020.3400E-030.1000E+01
AI1 1AJZ 1                   3 .5000E-02 .1000E-030.3400E-030.1000E+01

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

INCON -- INITIAL CONDITIONS FOR   20 ELEMENTS AT TIME   .216000E+03
A   1            .99000000E+00 1
  .1009978868521E+06  .1000000000000E-29  .1000000000000E-29  .2079000000000E+00
  .7821000000000E+00  .2000000000000E+02
A11 1            .35000000E+00 5
  .1009979673641E+06  .3059208923492E-02  .1521755161855E-01  .2044499533654E+00
  .2022859073864E+00  .2000000000000E+02
...
AI1 1            .35000000E+00 5
  .1009999987819E+06  .3104467422102E-02  .1501589504316E-01  .2041343842693E+00
  .9498977983169E-01  .2000000000000E+02
AJ  1            .99000000E+00 1
  .1010000000000E+06  .0000000000000E+00  .0000000000000E+00  .2079000000000E+00
  .7821000000000E+00  .2000000000000E+02

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.6.4. TMVOC input file for part 3 of problem 6 (redistribution).

```
...ITERATING...  AT [   1,  1] --- DELTEX =  .100000E+01   MAX. RES. =  .803738E-01  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   1,  2] --- DELTEX =  .100000E+01   MAX. RES. =  .732783E-03  AT ELEMENT A11 1  EQUATION   4
A11 1(   1,  3) ST =  .100000E+01 DT =  .100000E+01 DX1= -.627632E+00 DX2=  .187764E-07 T =  20.000 P =   100997. S =  .804066E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .116189E+00  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   2,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .124128E-02  AT ELEMENT A11 1  EQUATION   4
A11 1(   2,  3) ST =  .300000E+01 DT =  .200000E+01 DX1= -.170409E+00 DX2=  .472769E-08 T =  20.000 P =   100997. S =  .811974E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+01   MAX. RES. =  .158801E+00  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   3,  2] --- DELTEX =  .400000E+01   MAX. RES. =  .586284E-02  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   3,  3] --- DELTEX =  .400000E+01   MAX. RES. =  .155189E-04  AT ELEMENT AI1 1  EQUATION   4
AI1 1(   3,  4) ST =  .700000E+01 DT =  .400000E+01 DX1= -.438765E+00 DX2= -.285876E-05 T =  20.000 P =   101000. S =  .877850E+00
...ITERATING...  AT [   4,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .209680E+00  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   4,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .216806E-01  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   4,  3] --- DELTEX =  .800000E+01   MAX. RES. =  .100285E-03  AT ELEMENT AI1 1  EQUATION   4
AI1 1(   4,  4) ST =  .150000E+02 DT =  .800000E+01 DX1= -.755285E+00 DX2= -.342818E-05 T =  20.000 P =   100999. S =  .859051E+00
...ITERATING...  AT [   5,  1] --- DELTEX =  .160000E+02   MAX. RES. =  .268380E+00  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   5,  2] --- DELTEX =  .160000E+02   MAX. RES. =  .381750E-01  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   5,  3] --- DELTEX =  .160000E+02   MAX. RES. =  .723208E-04  AT ELEMENT AI1 1  EQUATION   4
AH1 1(   5,  4) ST =  .310000E+02 DT =  .160000E+02 DX1= -.113215E+01 DX2= -.140569E-05 T =  20.000 P =   100998. S =  .837102E+00
...ITERATING...  AT [   6,  1] --- DELTEX =  .320000E+02   MAX. RES. =  .326471E+00  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   6,  2] --- DELTEX =  .320000E+02   MAX. RES. =  .228972E-01  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   6,  3] --- DELTEX =  .320000E+02   MAX. RES. =  .138347E-03  AT ELEMENT AH1 1  EQUATION   5
A11 1(   6,  4) ST =  .630000E+02 DT =  .320000E+02 DX1= -.116124E+01 DX2=  .323539E-07 T =  20.000 P =   100994. S =  .860556E+00
...

 *rad3* .. air displacement of a NAPL from a lab. column (redistribut.)

         OUTPUT DATA AFTER (  18,  3)-2-TIME STEPS                                                                    THE TIME IS   .20000E+01 DAYS
@@@
```

```
*rad4* .. air displacement of a NAPL from a lab. column (airflooding)
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3     2650.      .350   8.4E-11   8.4E-11   8.4E-11       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .100       .08      .000       1.8
    8          0.000      2.00       40.       20.
ATMO2    3       10.      .990   8.4E-11   8.4E-11   8.4E-09       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .600       .05      .000        3.
    9

CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
...
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    5    5    3    8
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1

START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   3 200     20010003000000000 4 0004000                1.8
             7200.e0       -1.                       9.8065
     1.e+1
     1.E-5     1.E02                                1.000E-8                1.e4
    1
              1.000e5                0.00                0.0                0.00
                 0.99                20.0
...
TIMES----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    5
      900.     1740.     2700.     6000.     7200.
...
CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A   1A11 1                   3 .1000E-030.5000E-020.3400E-030.1000E+01
A11 1A21 1                   30.5000E-020.5000E-020.3400E-030.1000E+01
...
AH1 1AI1 1                   30.5000E-020.5000E-020.3400E-030.1000E+01
AI1 1AJZ 1                   3 .5000E-02 .1000E-030.3400E-030.1000E+01

FOFT
A11 1

INCON -- INITIAL CONDITIONS FOR   20 ELEMENTS AT TIME   .172800E+06
A   1            .99000000E+00 1
  .1009978868521E+06  .1000000000000E-29  .1000000000000E-29  .2079000000000E+00
  .7821000000000E+00  .2000000000000E+02
A11 1            .35000000E+00 5
  .1009958021192E+06  .3060462994415E-02  .1521229572868E-01  .2042400794138E+00
  .1058438889443E+00  .2000000000000E+02
...
GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AI1 1O2  1                       COM2  .27844e-5    300.e3
AI1 1N2  2                       COM3  .92155e-5    300.e3

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.6.6. TMVOC input file for part 4 of problem 6 (airflooding).

```
...ITERATING...  AT [   1,  1] --- DELTEX =  .100000E+02   MAX. RES. =  .636961E+02  AT ELEMENT A11 1  EQUATION   3
...ITERATING...  AT [   1,  2] --- DELTEX =  .100000E+02   MAX. RES. =  .935746E+01  AT ELEMENT A11 1  EQUATION   3
$$$ 5 ---> 7 $$$ WAT. EVOLVES AT ELEMENT *A11 1*  $$$   PS =   .49581E+04  PSAT=  .23366E+04
...ITERATING...  AT [   1,  3] --- DELTEX =  .100000E+02   MAX. RES. =  .357210E+01  AT ELEMENT AI1 1  EQUATION   3
$$$ 7 ---> 5 $$$ WAT. DISAPP. AT ELEMENT *A11 1*  $$$   PX =   .10103E+06  SG =   .89181E+00  SW =  -.14217E-02
...ITERATING...  AT [   1,  4] --- DELTEX =  .100000E+02   MAX. RES. =  .518428E+00  AT ELEMENT AI1 1  EQUATION   3
...ITERATING...  AT [   1,  5] --- DELTEX =  .100000E+02   MAX. RES. =  .576797E-02  AT ELEMENT A11 1  EQUATION   1
A11 1(   1,  6) ST =  .100000E+02 DT =  .100000E+02 DX1=  .342873E+02 DX2=  .118901E-04 T =  20.000 P =   101030. S =  .891001E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .100000E+02   MAX. RES. =  .179820E+00  AT ELEMENT AI1 1  EQUATION   5
...ITERATING...  AT [   2,  2] --- DELTEX =  .100000E+02   MAX. RES. =  .102024E-01  AT ELEMENT AI1 1  EQUATION   3
...ITERATING...  AT [   2,  3] --- DELTEX =  .100000E+02   MAX. RES. =  .294755E-02  AT ELEMENT AI1 1  EQUATION   3
...ITERATING...  AT [   2,  4] --- DELTEX =  .100000E+02   MAX. RES. =  .559897E-03  AT ELEMENT AI1 1  EQUATION   3
AH1 1(   2,  5) ST =  .200000E+02 DT =  .100000E+02 DX1=  .666474E+00 DX2=  .671479E-05 T =  20.000 P =   102168. S =  .778669E+00
...
*rad4* .. air displacement of a NAPL from a lab. column (airflooding)

         OUTPUT DATA AFTER (  93,  4)-2-TIME STEPS                                                                    THE TIME IS   .31250E-01 DAYS
@@@
```

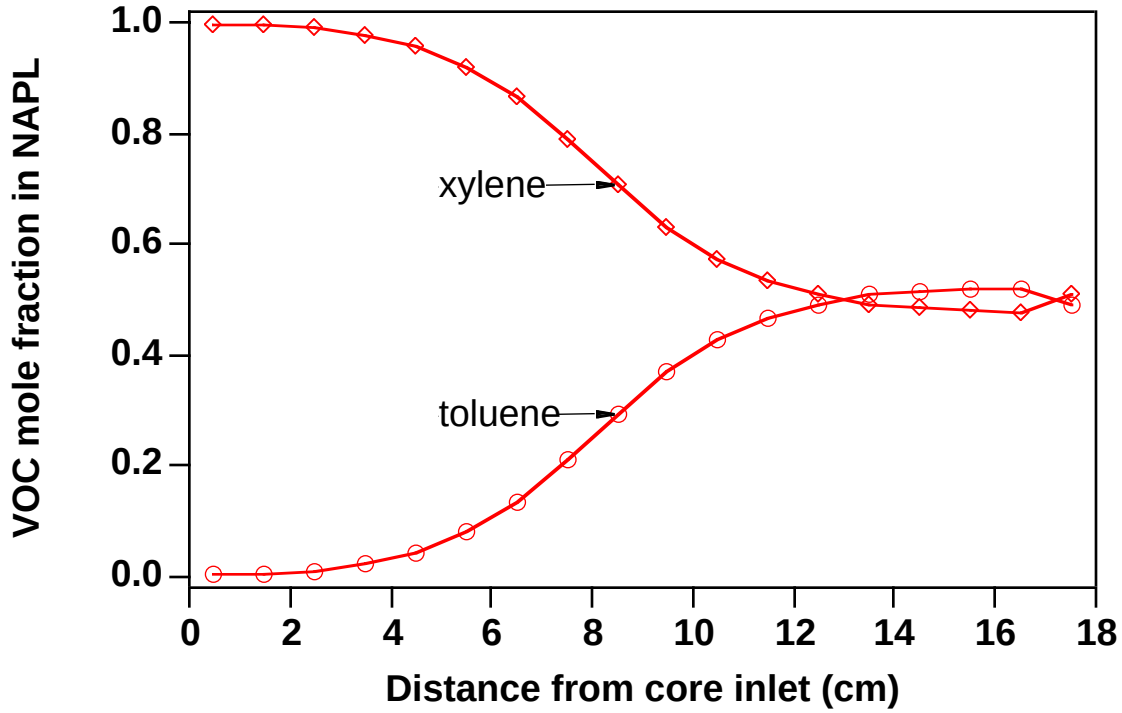


Figure 10.6.8. o-xylene and toluene concentrations in the NAPL phase after 1740 s (29 min) of air flooding.

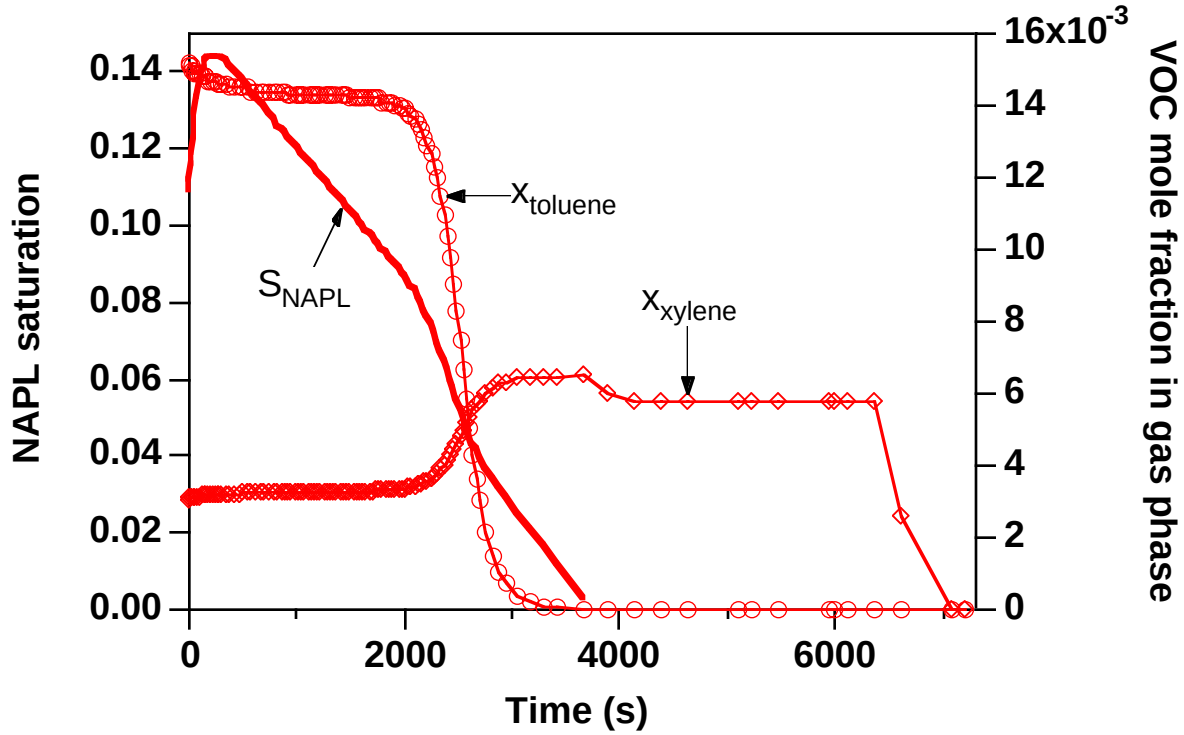


Figure 10.6.9. o-xylene and toluene concentrations in the gas phase and NAPL saturation in the uppermost element as a function of time during the air flooding.

10.7 Problem No. 7 (*r2dl*) - NAPL Spill in the Unsaturated Zone

This simulation demonstrates the application of TMVOC to a flow problem with realistic features as would be encountered in actual field situations. We consider a multicomponent NAPL spill in the unsaturated zone that is followed by redistribution of the NAPL plume within the unsaturated zone and along the water table. Subsequent remediation operations involve VOC recovery from the unsaturated zone by soil vapor extraction close to the spill area and NAPL extraction by pumping from the saturated zone. We include a discussion of the approach for preparing initial and boundary conditions, including atmospheric conditions at the land surface, recharge across the vadose zone due to infiltration at the land surface, and natural flow in the unconfined aquifer.

We consider a two-dimensional vertical section of 1 m thickness that is oriented parallel to the direction of flow in the aquifer. The section is 100 m long and extends from the land surface to a depth of 15 m (Fig. 10.7.1). Depth to water table is 5 m on the left side of the section and 5.5 m

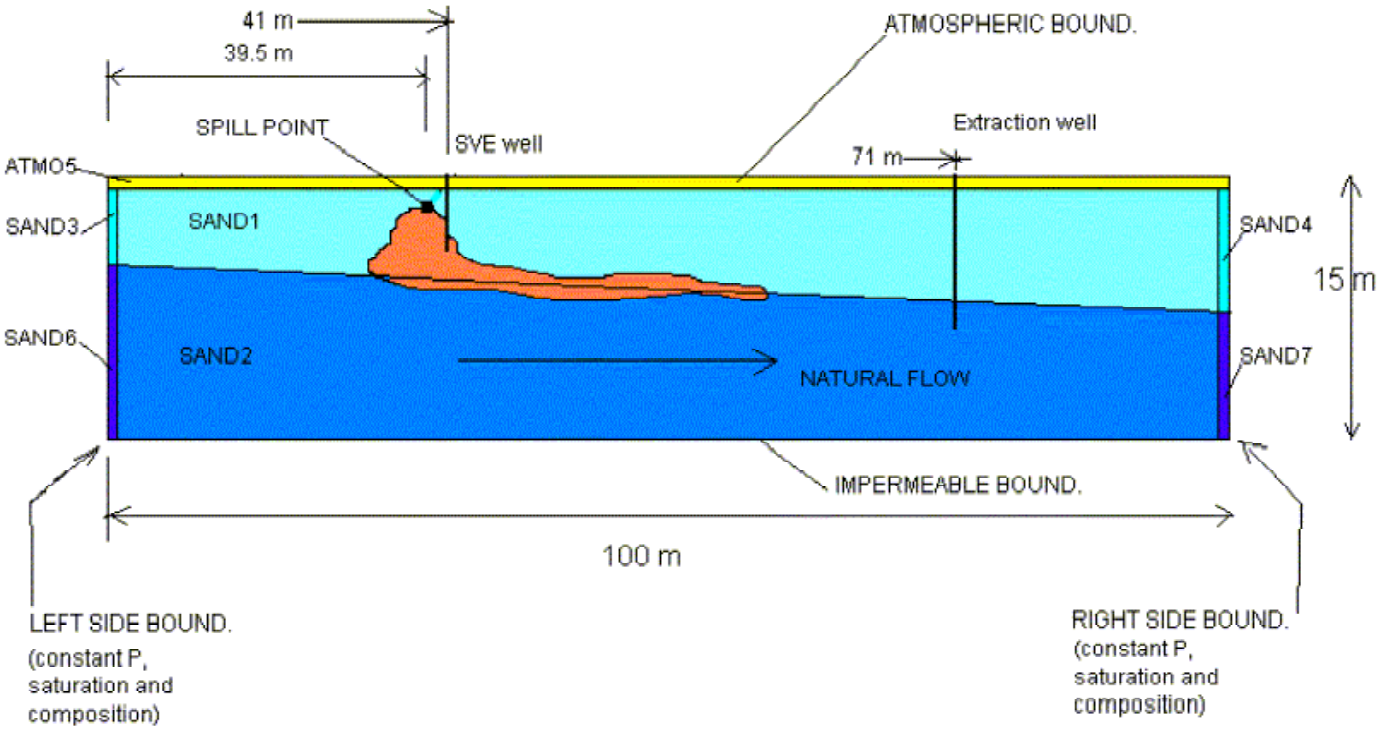


Figure 10.7.1. Conceptual model of 2-D vertical section problem for simulating a multicomponent NAPL spill in the unsaturated zone. Rock domain assignments and boundary conditions are shown together with the position of the spill point, a SVE well, and a downstream extraction well.

on the right side, resulting in flow from left to right in the aquifer with a pore velocity of 18.9 m/yr. A 2-D Cartesian grid is used, consisting of 40 columns and 17 layers for a total of 680 elements. The MESHMAKER data for generating the computational grid and a grid diagram are shown in Figs. 10.7.2 and 10.7.3, respectively. Vertical grid spacing is 0.5 m in the unsaturated zone and in the upper part of the unconfined aquifer. Horizontal grid spacing is 1 m in the region affected by the NAPL spill and the subsequent soil vapor extraction, and gradually increases to 10 m near the left and right boundaries.

```
MESHMAKER1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
XYZ

NX       1     0.001
NX       2      10.0
NX       2       5.0
NX       4       2.0
NX      16       1.0
NX      10       2.0
NX       1       3.0
NX       1       5.0
NX       1       8.0
NX       1      10.0
NX       1     0.001
NY       1       1.0
NZ       1     0.001
NZ      12       0.5
NZ       1       1.0
NZ       2       2.0
NZ       1       4.0

ENDFI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.7.2. MESHMAKER input data for 2-D vertical section grid.

The problem is run in four segments, (1) generation of steady flow prior to introduction of NAPL, (2) NAPL spill in the unsaturated zone, (3) redistribution of NAPL, and (4) extraction simultaneously in the saturated and unsaturated zones. The preparation of input data for the steady state equilibration run of the 2-D grid consisted of the following steps:

- generation of the 2-D grid using the MESHMAKER facility for Cartesian grids available within TMVOC. Small changes were made in subroutine GXYZ of the MESHMAKER module meshm.f to obtain the domain assignments as shown in Fig. 10.7.1.
- generation of left side boundary conditions using column 1 of the 2-D grid and running to gravity-capillary equilibrium. For this, atmospheric conditions were assigned to the topmost element, and single-phase water conditions with an appropriate pressure were assigned to the first element in the saturated zone in order to fix the water table elevation. The pressure-controlling grid blocks were made inactive for this run.

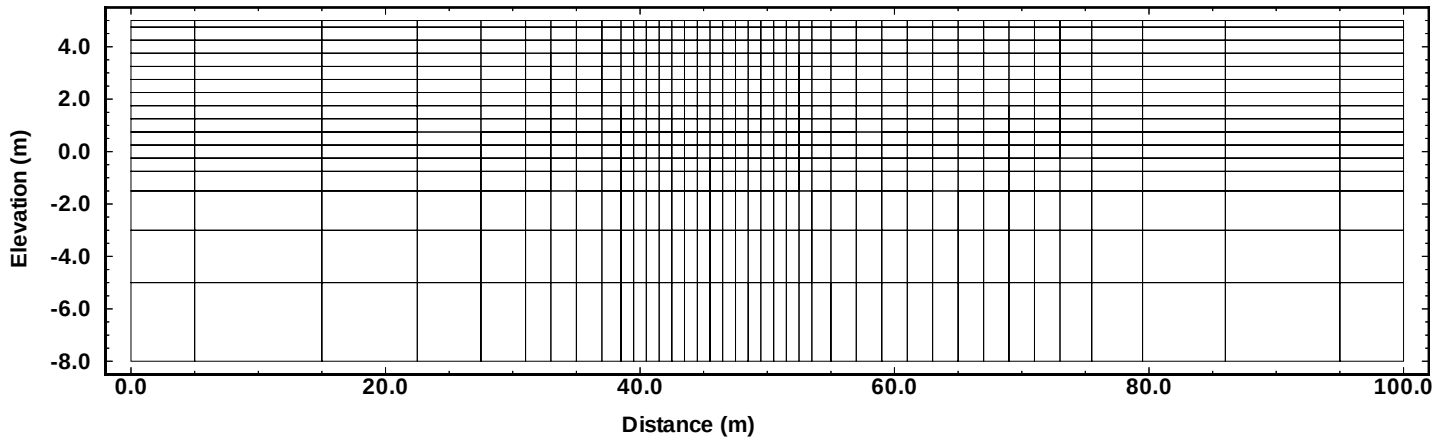


Figure 10.7.3. Grid diagram for 2-D vertical section model. Note the large vertical exaggeration. The lines shown are connections between nodal points. The water table is near elevation 0.0.

- generation of right side boundary conditions using column 40 of the 2-D grid, following the same procedure as described for the left boundary.

Fig. 10.7.4 shows the input file *r2dl1* used for generating the "natural" state prior to the contamination event. Although soil properties are homogeneous throughout, different portions of the flow domain are assigned to different material domains (Fig. 10.7.1). This was done to facilitate generation of initial conditions for representing steady flow prior to the NAPL spill. Typical parameters were used for porosity (30 %) and permeability (4×10^{-12} m^2 ≈ 4 darcy horizontally, 1×10^{-12} m^2 ≈ 1 darcy vertically). The capillary pressure functions follow the Parker et al. (1987) model, and relative permeability curves are given by a modified version of the Stone I model (Stone, 1970).

File *r2dl1* includes the INCON data generated for the left (A...1) and right (A..40) boundary columns, and also includes INDOM data for domains SAND1 (unsaturated zone), SAND2 (saturated zone), and ATMO5 (atmosphere). The left and right columns of the grid were made inactive, to maintain constant boundary conditions. The top row of grid blocks belongs to domain ATMO5 and also was made inactive, maintaining constant atmospheric conditions there. The SAND1 and SAND2 INDOM-data simply provide convenient starting values for the run. GENER-data specify a net infiltration of 10 cm/year of water (COM1) across the top of the model (second row of grid blocks). The rates were obtained by converting the 10 cm/yr volumetric rate into a mass rate, using $\rho_w \approx 998.32$ kg/m^3 at T = 20 °C and ambient pressure, and taking into

account the footprint areas of the grid blocks. No specification of injection enthalpy is needed because the run is made in isothermal mode (NEQ = NK).

All runs prior to the NAPL spill are performed with NK= 2 specified in data block MULTI, for a flow system with only two fluid components (water and air). No parameters for calculating chemical and transport properties of hydrocarbons are needed for NK = 2, so data block CHEMP consists of just a single record with NHC = 0. We include multicomponent diffusion by specifying NB = 8 in MULTI. Tortuosities in all domains are set to zero, which means that the Millington-Quirk model (Eq. D.5) will be used. Data block DIFFU includes only two records, the first giving diffusivities for water, the second for air.

The *r2dl1* run terminates automatically when steady-state criteria are satisfied. A portion of the printed output is shown in Fig. 10.7.5. The numerically most difficult aspect of this problem is that, because of different water table elevations at the left and right boundaries, some grid blocks in grid layer C are very close to the phase boundary. In our simulation, grid blocks AC1 2 through AC121 remain in single-phase liquid conditions, while grid blocks AC122 through AC139 end up in two-phase conditions, with water saturations declining monotonically from S_w = .99946 in AC122 to .66982 in AC139.

The next run segment (*r2dl2*) simulates a NAPL spill, which requires several modifications in the input file (Fig. 10.7.6). Data for six VOCs are introduced through data block CHEMP. In MULTI we now specify NK = 8 components (water, air, and 6 VOCs), and we set NKIN = 2, to be able to initialize the run from the thermodynamic conditions for the two-component water-air system that were obtained in the first run segment. The SAVE file from the first run segment (r2dl1) is used as file INCON, but we first replace the second last line(+++) with a blank line, so that simulation time and time step counter will be reset to zero. In PARAM a maximum simulation time of TIMAX = 31.5576e6 s = 365.25 days = 1 year is specified. Block DIFFU now has 8 records with diffusivities for all fluid components. In block GENER the water sources for infiltration at the land surface are kept, and 6 sources are added for the VOCs that specify different mass rates. VOC injection is made into grid block A3111 (x = 39.5 m, z = 4.25 m). The ordering of these sources is arbitrary. We also include an FOFT-block, to generate time series of parameters in three different grid blocks.

The desired simulation time for the spill problem is reached after 120 time steps. Some of the printed output is shown in Fig. 10.7.7, and Fig. 10.7.8 shows a contour plot of total VOC mass fraction in the aqueous phase at 1 yr. The differences in volatility and solubility of the different

NAPL components give rise to interesting compositional effects. For example, the NAPL phase in the injection grid block A3111 has a much larger concentration of n-pentane than in neighboring grid block A3110, while all other component concentrations are smaller. The total VOC mass fraction dissolved in water is actually slightly larger in the grid blocks that are laterally offset from the source block than in the source block itself. In the vadose zone, the VOCs have spread almost symmetrically around the spill point by gas diffusion, as well as by advection driven by the larger density of NAPL vapors. In the saturated zone a plume of dissolved VOCs is being dragged to the right by the "natural" flow in the aquifer.

The third run segment simulates redistribution of the VOCs, using the SAVE file written at the end of the spill period as INCON. We again replace the second last line of file SAVE with a blank line, to reset time and iteration counters. Minor modifications are required in the input file (Fig. 10.7.9). The specification NKIN = 2 in MULTI is removed, because the run is now initialized with data for NK = 8 components. Some different iteration and time step controls are used in block PARAM, including maximum number of iterations NOITE = 4, and doubling of time step only when convergence is achieved in no more than 3 iterations (parameter MOP(16)). These modifications are not essential, but were made because test calculations showed that permitting more aggressive time step growth and a larger number of Newtonian iterations seldom resulted in successful time steps. Some printed output is shown in Fig. 10.7.10, and Figs. 10.7.11 and 10.7.12 show contour diagrams of, respectively, mass fractions of VOC dissolved in the aqueous phase, and NAPL phase saturation.

Comparing Fig. 10.7.11 with Fig. 10.7.8 at the end of the spill period, it is seen that the VOC plume has increased in volume, and dissolved VOCs have penetrated deeper into the saturated zone. NAPL saturations in the upper part of the unsaturated zone are now slightly below the irreducible value of 0.05, having first been lowered by gravity drainage and subsequently, after S_o = 0.05 has been reached, by volatilization and dissolution. A NAPL lense is floating on the water table (grid layer C). Total VOC inventory during the redistribution period declines from an initial value of 867.24 kg to a final value of 822.06 kg. This reduction occurs primarily through vapor diffusion across the land surface; small amounts of VOCs also leave the flow system by advection across the right boundary.

The final segment of this problem models extraction of VOCs. GENER-data in the input file (Fig. 10.7.13) were modified to include a soil vapor extraction well "SVE 1", which produces on deliverability against a sandface pressure of 0.9×10^5 Pa from grid layers 4 through 8. Another extraction well produces from the saturated zone (grid blocks AD134 and AE134). We also include

FOFT and GOFT-data to generate time series of selected parameters for plotting. At the end of the simulation, 470.48 kg of VOCs, corresponding to 54.3 % of the original inventory, are remaining in the flow system (Fig. 10.7.14). Approximately 99.8 % of this inventory is present as a free NAPL phase, 0.18 % is dissolved in water, and 0.02 % is in the gas phase. The spatial extent of VOC contamination has been much reduced, compare Figs. 10.7.15 and 10.7.11.

Fig. 10.7.16 shows the evolution of NAPL saturations at selected locations, plotted from the FOFT file generated by the extraction simulation. NAPL inventory in the vadose zone is very effectively reduced by the soil vapor extraction, and NAPL phase disappears from grid blocks A3111 (x = 39.5 m, z = 4.25 m) and A8111 (x = 39.5 m, z = 1.75 m). Saturation of the NAPL lense floating on the water table (near z = - 0.25 m) is reduced much more slowly. In the vadose zone, dissolved VOC mass fractions in the aqueous phase decrease rapidly at high elevations, and more slowly near the water table (Fig. 10.7.17). Dissolved VOC concentrations at and below the water table show only very weak reductions.

```
*r2dl1* ... get steady state for 2D-section of sat.-unsat. system with recharge
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84        10.       11.
SAND2    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84        10.       11.
SAND3    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84        10.       11.
SAND4    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84        10.       11.
ATMO5    3     2650.      .999   4.0E-09   4.0E-09   1.0E-09       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .600       .01      .000        3.
    9
SAND6    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84        10.       11.
SAND7    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1    50000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84        10.       11.

CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
AIR
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2    2    3    8
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   3 120     12010003000000000 4 0000000                1.8
          3.1536E14       -1.                       9.8060
     1.e+0
     1.E-6     1.E02                                1.000E-8              1.E+4
    2
             1.010e5              0.9E-7                20.0
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
```

Figure 10.7.4. Portion of TMVOC input file for part 1 of problem 7 (obtaining steady-state conditions prior to NAPL spill).

```
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .100       .05      .001       3.0
    8          0.000      1.84       10.       11.
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
     2.e-5    6.e-10    6.e-10
     2.e-5    6.e-10    6.e-10
INDOM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    4
 0.1010204333370E+06 0.2000123526968E+00 0.2000000000000E+02
SAND2    2
 0.1156839936204E+06 0.9399999999818E-05 0.2000000000000E+02
ATMO5    1
 0.1010000000000E+06 0.9900000000000E+00 0.2000000000000E+02

INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A21 1             .30000000E+00 4
  .1010029303117E+06  .2000069202348E+00  .2000000000000E+02
A31 1             .30000000E+00 4
  .1010087651609E+06  .2000091681103E+00  .2000000000000E+02
...
AB1 1             .30000000E+00 4
  .1010554561999E+06  .6340472776461E+00  .2000000000000E+02
AC1 1             .30000000E+00 2
  .1034470067655E+06  .9000000000281E-05  .2000000000000E+02
AD1 1             .30000000E+00 2
  .1083417960312E+06  .8999999999995E-05  .2000000000000E+02
...
A2140             .30000000E+00 4
  .1010029303117E+06  .2000073764287E+00  .2000000000000E+02
...
AB140             .30000000E+00 4
  .1010554561999E+06  .3039224987121E+00  .2000000000000E+02
AC140             .30000000E+00 4
  .1010612941108E+06  .6332639228686E+00  .2000000000000E+02
AD140             .30000000E+00 2
  .1034470075043E+06  .9000000028229E-05  .2000000000000E+02
...

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A21 2RAI02                         COM1 3.1650E-05
A21 3RAI03                         COM1 3.1650E-05
A21 4RAI04                         COM1 1.5825E-05
...
A2135RAI35                         COM1 6.3300E-06
A2136RAI36                         COM1 9.4950E-06
A2137RAI37                         COM1 1.5825E-05
A2138RAI38                         COM1 2.5320E-05
A2139RAI39                         COM1 3.1650E-05

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.7.4. Portion of TMVOC input file for part 1 of problem 7 (continued).

```
 ...ITERATING...  AT [   1,  1] --- DELTEX =  .100000E+01   MAX. RES. =  .148154E-02  AT ELEMENT AB1 2  EQUATION   1
 ...ITERATING...  AT [   1,  2] --- DELTEX =  .100000E+01   MAX. RES. =  .668547E-03  AT ELEMENT AC122  EQUATION   2
 $$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AC1 3*  $$$   PX =   .93282E+05  PG =   .97653E+05
 $$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AC1 8*  $$$   PX =   .94039E+05  PG =   .95009E+05
 $$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AC1 9*  $$$   PX =   .94033E+05  PG =   .95030E+05
...
 $$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AC138*  $$$   PX =   .93289E+05  PG =   .97629E+05
 $$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AC139*  $$$   PX =   .93895E+05  PG =   .95580E+05
 ...ITERATING...  AT [   1,  3] --- DELTEX =  .100000E+01   MAX. RES. =  .100043E-03  AT ELEMENT AC1 3  EQUATION   2
 $$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AC1 4*  $$$   PX =   .93170E+05  PG =   .98049E+05
 $$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AC1 5*  $$$   PX =   .93108E+05  PG =   .98266E+05
...
 ...ITERATING...  AT [   1,  4] --- DELTEX =  .100000E+01   MAX. RES. =  .117789E-03  AT ELEMENT AC1 5  EQUATION   2
 AC1 5(   1,  5) ST =  .100000E+01 DT =  .100000E+01 DX1= -.214409E+05 DX2=  .999973E+00 T =  20.000 P =    94243. S =  .179116E-04
 ...ITERATING...  AT [   2,  1] --- DELTEX =  .100000E+01   MAX. RES. =  .541521E-03  AT ELEMENT AC122  EQUATION   2
 $$$ 2 ---> 4 $$$ GAS  EVOLVES AT ELEMENT *AC1 2*  $$$   PX =   .93134E+05  PG =   .11984E+06
 ...ITERATING...  AT [   2,  2] --- DELTEX =  .100000E+01   MAX. RES. =  .610349E-03  AT ELEMENT AC1 2  EQUATION   2
 ...ITERATING...  AT [   2,  3] --- DELTEX =  .100000E+01   MAX. RES. =  .267091E-05  AT ELEMENT AC1 2  EQUATION   2
 AC1 2(   2,  4) ST =  .200000E+01 DT =  .100000E+01 DX1=  .466769E+04 DX2=  .999891E+00 T =  20.000 P =    99000. S =  .968211E-04
 ...ITERATING...  AT [   3,  1] --- DELTEX =  .200000E+01   MAX. RES. =  .819678E-03  AT ELEMENT AB139  EQUATION   1
 ...ITERATING...  AT [   3,  2] --- DELTEX =  .200000E+01   MAX. RES. =  .513404E-05  AT ELEMENT AB139  EQUATION   1
 AB139(   3,  3) ST =  .400000E+01 DT =  .200000E+01 DX1=  .425121E+02 DX2=  .192203E-03 T =  20.000 P =   100493. S =  .799696E+00
 ...ITERATING...  AT [   4,  1] --- DELTEX =  .400000E+01   MAX. RES. =  .192939E-02  AT ELEMENT AB1 2  EQUATION   1
 ...ITERATING...  AT [   4,  2] --- DELTEX =  .400000E+01   MAX. RES. =  .186150E-05  AT ELEMENT AB1 2  EQUATION   1
 AE122(   4,  3) ST =  .800000E+01 DT =  .400000E+01 DX1=  .263861E+04 DX2=  .265513E-13 T =  20.000 P =   109200. S =  .000000E+00
 ...ITERATING...  AT [   5,  1] --- DELTEX =  .800000E+01   MAX. RES. =  .389779E-02  AT ELEMENT AB1 2  EQUATION   1
 ...ITERATING...  AT [   5,  2] --- DELTEX =  .800000E+01   MAX. RES. =  .368643E-05  AT ELEMENT AB139  EQUATION   1
 AD127(   5,  3) ST =  .160000E+02 DT =  .800000E+01 DX1=  .917369E+03 DX2=  .231469E-09 T =  20.000 P =   104799. S =  .000000E+00
...

 *r2dl1* ... get steady state for 2D-section of sat.-unsat. system with recharge

          OUTPUT DATA AFTER (  106,  1)-2-TIME STEPS                                                    THE TIME IS   .79683E+07 DAYS
@@@
```

```
*r2dl2* ... multicomponent NAPL spill in unsaturated zone
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84       10.       11.
...
CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6
n-DECANE
   617.700    21.200     0.249     0.489      0.00
   447.300  -8.56523   1.97756  -5.81971  -0.29982
   142.286 -7.913E+0  9.609E-1 -5.288E-4  1.131E-7
   730.000   293.000  1.000E-5   293.000     1.600
                       0.5900   293.000   603.000
  3.799e-7
     7.000     0.001
BENZENE
     562.2      48.2     0.271     0.212       0.0
     353.2  -6.98273   1.33213  -2.62863  -3.33399
...
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    8    8    3    8    2
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   3 999     99910000000000000 4 0000000                 1.8
           31.5576e6      -1.                       9.8060
     1.e+1
     1.E-5     1.E02                                1.000E-8                1.e4
    2
             1.010e5              0.9E-7                 20.0
...
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
     2.e-5    6.e-10    6.e-10
     2.e-5    6.e-10    6.e-10
    8.0e-6    6.e-10    6.e-10
...
GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A21 2RAI02                        COM1 3.1650E-05
...
A2139RAI39                        COM1 3.1650E-05
A3111HC  1                        COM8   7.50E-06
A3111HC  2                        COM4   3.00E-07
A3111HC  3                        COM5   1.80E-06
A3111HC  4                        COM6   3.00E-06
A3111HC  5                        COM7   3.00E-06
A3111HC  6                        COM3   1.44E-05

FOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A3111
AC111
AC115

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.7.6. Portion of TMVOC input file for part 2 (NAPL spill) of problem 7.

```
...ITERATING...  AT [   1,  1] --- DELTEX =  .100000E+02   MAX. RES. =  .207897E-04  AT ELEMENT A3111  EQUATION   8
A3111(   1,  2) ST =  .100000E+02 DT =  .100000E+02 DX1=  .143750E+02 DX2=  .192620E-03 T =  20.000 P =   101024. S =  .745406E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+02   MAX. RES. =  .625337E-04  AT ELEMENT A3111  EQUATION   2
A3111(   2,  2) ST =  .300000E+02 DT =  .200000E+02 DX1=  .704983E+01 DX2=  .384571E-03 T =  20.000 P =   101031. S =  .745404E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+02   MAX. RES. =  .164925E-03  AT ELEMENT A3111  EQUATION   2
...ITERATING...  AT [   3,  2] --- DELTEX =  .400000E+02   MAX. RES. =  .165668E-04  AT ELEMENT A3111  EQUATION   2
A3111(   3,  3) ST =  .700000E+02 DT =  .400000E+02 DX1=  .165322E+01 DX2=  .744823E+00 T =  20.000 P =   101032. S =  .745400E+00
...
*r2dl2* ... multicomponent NAPL spill in unsaturated zone

         OUTPUT DATA AFTER (  120,  5)-2-TIME STEPS                                                    THE TIME IS   .36525E+03 DAYS
@@@
```

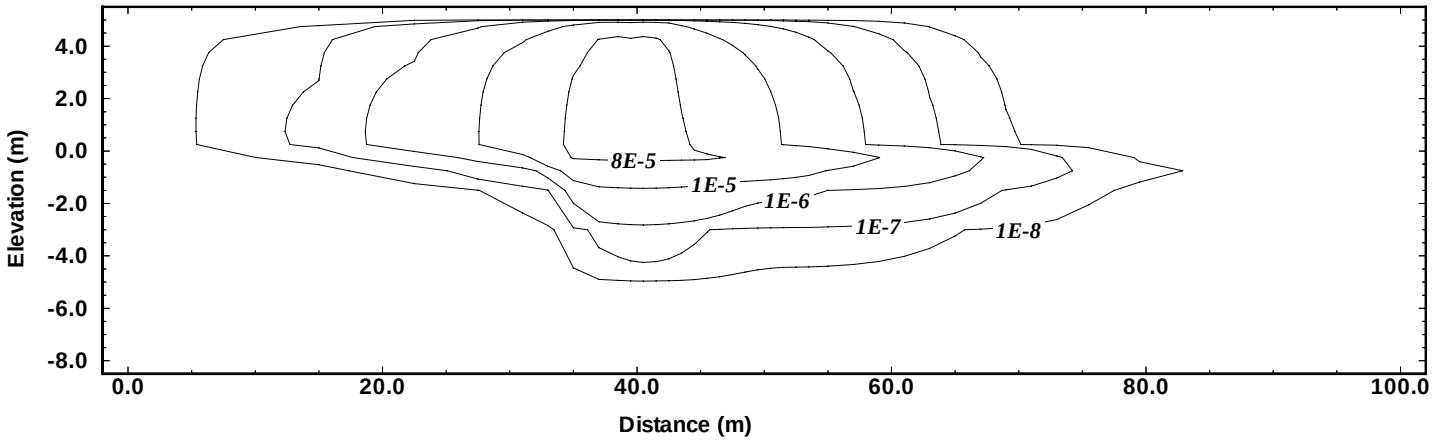


Figure 10.7.8. Contour plot of total VOC mass fraction in the aqueous phase at the end of the NAPL spill period.

```
*r2dl3* ... redistribution of NAPL for 1 year following spill
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84       10.       11.
...
MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    8    8    3    8
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
 4 3 999     99910000000000000 3 0000000                1.8
           31.5576e6      -1.                       9.8060
     1.e+2
     1.E-5     1.E02                                1.000E-8                1.e4
    4
  .1010204333370E+06  .0000000000000E+00  .0000000000000E+00  .0000000000000E+00
  .0000000000000E+00  .0000000000000E+00  .0000000000000E+00  .2000123526968E+00
  .2000000000000E+02
...
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6           .100       .05      .001       3.0
    8          0.000      1.84       10.       11.
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
     2.e-5    6.e-10    6.e-10
     2.e-5    6.e-10    6.e-10
    8.0e-6    6.e-10    6.e-10
    7.7e-6    6.e-10    6.e-10
    8.8e-6    6.e-10    6.e-10
    7.1e-6    6.e-10    6.e-10
    8.0e-6    6.e-10    6.e-10
    7.7e-6    6.e-10    6.e-10
TIMES----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
  1.5768E7
GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A21 2RAI02                        COM1 3.1650E-05    300.E3
...
A2138RAI38                        COM1 2.5320E-05    300.E3
A2139RAI39                        COM1 3.1650E-05    300.E3

FOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A3111
AC111
AC115
AC120

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.7.9. Portion of TMVOC input file for part 3 (NAPL redistribution) of problem 7.

```
 ...ITERATING...  AT [   1,  1] --- DELTEX =  .100000E+03   MAX. RES. =  .198675E-03  AT ELEMENT A3111  EQUATION   8
 A3111(   1,  2) ST =  .100000E+03 DT =  .100000E+03 DX1= -.235059E+00 DX2=  .273703E-04 T =  20.000 P =   101015. S =  .603859E+00
 ...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+03   MAX. RES. =  .395836E-03  AT ELEMENT A3111  EQUATION   8
 A3111(   2,  2) ST =  .300000E+03 DT =  .200000E+03 DX1= -.290568E-01 DX2=  .546485E-04 T =  20.000 P =   101015. S =  .603914E+00
 ...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+03   MAX. RES. =  .790640E-03  AT ELEMENT A3111  EQUATION   8
 A3111(   3,  2) ST =  .700000E+03 DT =  .400000E+03 DX1= -.562347E-02 DX2=  .108943E-03 T =  20.000 P =   101015. S =  .604023E+00
 ...ITERATING...  AT [   4,  1] --- DELTEX =  .800000E+03   MAX. RES. =  .157779E-02  AT ELEMENT A3111  EQUATION   8
 A3111(   4,  2) ST =  .150000E+04 DT =  .800000E+03 DX1= -.172260E-02 DX2=  .216485E-03 T =  20.000 P =   101015. S =  .604239E+00
 ...ITERATING...  AT [   5,  1] --- DELTEX =  .160000E+04   MAX. RES. =  .314181E-02  AT ELEMENT A3111  EQUATION   8
 A3111(   5,  2) ST =  .310000E+04 DT =  .160000E+04 DX1= -.153440E-03 DX2=  .427468E-03 T =  20.000 P =   101015. S =  .604667E+00
...

 *r2dl3* ... redistribution of NAPL for 1 year following spill

          OUTPUT DATA AFTER (  248,  3)-2-TIME STEPS                                                    THE TIME IS   .36525E+03 DAYS
@@@
```

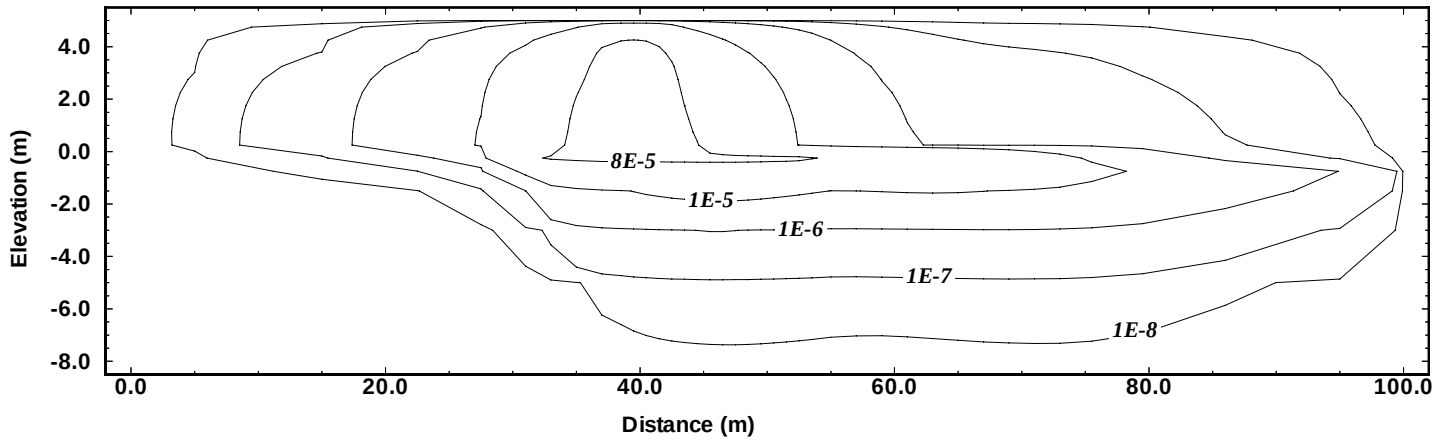


Figure 10.7.11. Contour plot of total VOC mass fraction in the aqueous phase at the end of the NAPL redistribution period.

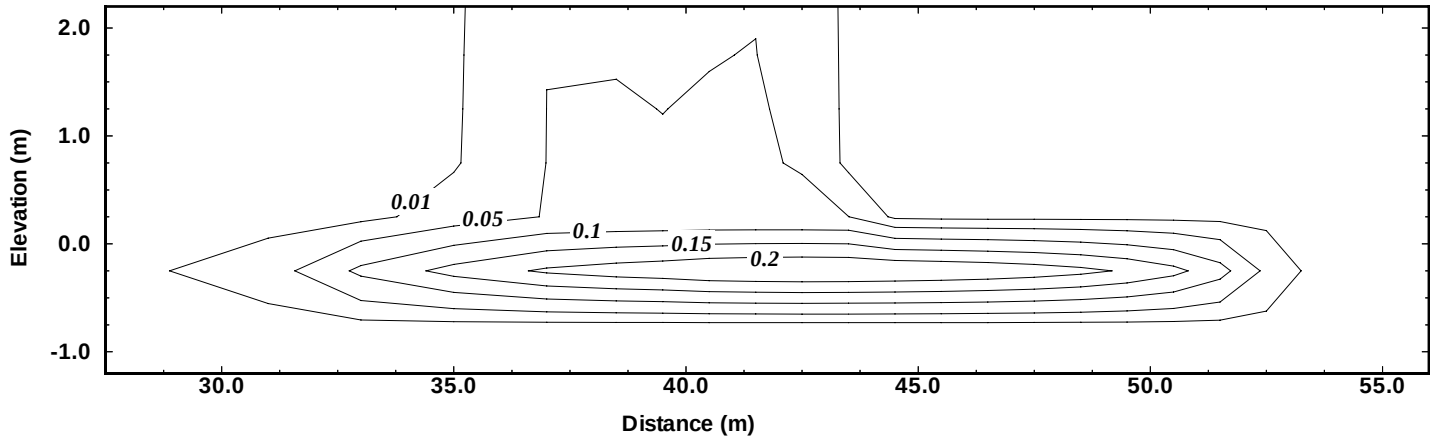


Figure 10.7.12. NAPL saturations at the end of the redistribution period.

```
*r2dl4 ... SVE and water extraction following NAPL redistribution
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3     2650.      .300   4.0e-12   4.0e-12   1.0e-12       3.1     1000.
     0.e-8        0.      2.85       0.0
    6           .200       .05      .010       3.0
    8          0.000      1.84       10.       11.
...
GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A21 2RAI02                        COM1 3.1650E-05
A21 3RAI03                        COM1 3.1650E-05
...
A2139RAI39                        COM1 3.1650E-05
A8113SVE 1                   5    DELV   1.00E-11                0.5
A7113SVE 1                        DELV   1.00E-11                0.5
A6113SVE 1                        DELV   1.00E-11                0.5
A5113SVE 1                        DELV   1.00E-11                0.5
A4113SVE 1                        DELV   1.00E-11    0.90E5      0.5
AE134WEL 1                   2    DELV   5.00E-12                0.5
AD134WEL 1                        DELV   5.00E-12    1.01E5      0.5

FOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A3111
A8111
AC111
AC115
AC120
AE134
AD134

GOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AE134WEL 1                   2    DELV   5.00E-12                0.5
AD134WEL 1                        DELV   5.00E-12    1.01E5      0.5

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 10.7.13. Portion of TMVOC input file for part 4 (extraction) of problem 7.

```
********** VOLUME- AND MASS-BALANCES **********************************************************************************************

********** [KCYC,ITER] = [   0,  0] *****                                    THE TIME IS   .00000E+00 SECONDS, OR   .00000E+00 DAYS

PHASES                      GAS            AQUEOUS           NAPL            TOTAL

VOLUMES     (m**3)     .10926797E+03     .33963568E+03     .10963533E+01     .45000000E+03
MASS       (moles)     .45313642E+04     .18820521E+08     .71573897E+04     .18832210E+08
ENERGY         (J)    -.24675334E+07     .28431344E+11     .31158402E+08     .84110035E+11

                        COMPONENTS MOLES IN PLACE - BY PHASES                          COMPONENTS IN PLACE - OVERALL

COMPONENTS              GAS PHASE       AQUEOUS PHASE         NAPL           ADSORBED        TOTAL MOLES     TOTAL MASS (kg)
WATER                  .10479869E+03     .18820320E+08     .18119199E+01                     .18820427E+08     .33906881E+06
AIR                    .43865636E+04     .18663480E+03     .61335548E-01                     .45732598E+04     .13244160E+03
n-DECANE               .42699165E+00     .15010276E+00     .31765404E+04     .00000000E+00     .31771175E+04     .45205934E+03
BENZENE                .62314098E+00     .42292829E+01     .97011376E+02     .00000000E+00     .10186380E+03     .79569889E+01
Toluene                .12211053E+01     .63137007E+01     .56339194E+03     .00000000E+00     .57092674E+03     .52605761E+02
4-p-XYLENE             .66000692E+00     .30030992E+01     .86656628E+03     .00000000E+00     .87022938E+03     .92390513E+02
n-propylbenzene        .24613701E+00     .84054929E+00     .77731937E+03     .00000000E+00     .77840606E+03     .93560516E+02
n-pentane              .36824514E+02     .16182845E-01     .16746871E+04     .00000000E+00     .17115278E+04     .12348844E+03
total VOCs             .40001896E+02     .14552918E+02     .71555165E+04     .00000000E+00     .72100713E+04     .82206156E+03

**********************************************************************************************************************************

...ITERATING...  AT [   1,  1] --- DELTEX =  .100000E+02   MAX. RES. =  .337435E-01  AT ELEMENT A8113  EQUATION   2
...ITERATING...  AT [   1,  2] --- DELTEX =  .100000E+02   MAX. RES. =  .432680E+00  AT ELEMENT A2113  EQUATION   2
A7113(   1,  3) ST =  .100000E+02 DT =  .100000E+02 DX1= -.683620E+04 DX2=  .243494E-04 T =  20.000 P =    94200. S =  .699088E+00
...ITERATING...  AT [   2,  1] --- DELTEX =  .200000E+02   MAX. RES. =  .118947E-01  AT ELEMENT A6113  EQUATION   2
...ITERATING...  AT [   2,  2] --- DELTEX =  .200000E+02   MAX. RES. =  .232348E-01  AT ELEMENT A2119  EQUATION   2
AB116(   2,  3) ST =  .300000E+02 DT =  .200000E+02 DX1= -.185343E+03 DX2= -.630216E-05 T =  20.000 P =   100856. S =  .557975E+00
...ITERATING...  AT [   3,  1] --- DELTEX =  .400000E+02   MAX. RES. =  .387284E-02  AT ELEMENT A6112  EQUATION   2
$$$ 6 ---> 7 $$$ GAS  EVOLVES AT ELEMENT *AC112*  $$$   PX =   .10164E+06  PG =  .10271E+06
$$$ 6 ---> 7 $$$ GAS  EVOLVES AT ELEMENT *AC113*  $$$   PX =   .10153E+06  PG =  .10267E+06
$$$ 6 ---> 7 $$$ GAS  EVOLVES AT ELEMENT *AC114*  $$$   PX =   .10156E+06  PG =  .10275E+06
...ITERATING...  AT [   3,  2] --- DELTEX =  .400000E+02   MAX. RES. =  .167617E-01  AT ELEMENT A2123  EQUATION   2
...ITERATING...  AT [   3,  3] --- DELTEX =  .400000E+02   MAX. RES. =  .154993E-04  AT ELEMENT AC110  EQUATION   1
AC110(   3,  4) ST =  .700000E+02 DT =  .400000E+02 DX1= -.288095E+03 DX2=  .632337E-04 T =  20.000 P =   102196. S =  .354727E-02
...ITERATING...  AT [   4,  1] --- DELTEX =  .800000E+02   MAX. RES. =  .263118E-02  AT ELEMENT A7112  EQUATION   2
$$$ 4 ---> 7 $$$ NAPL EVOLVES AT ELEMENT *AB117*  $$$   xsumoil=   .16119E+01
...ITERATING...  AT [   4,  2] --- DELTEX =  .800000E+02   MAX. RES. =  .423990E-01  AT ELEMENT A2126  EQUATION   2
AB118(   4,  3) ST =  .150000E+03 DT =  .800000E+02 DX1= -.784433E+03 DX2=  .353228E-03 T =  20.000 P =    99898. S =  .566067E+00
...

*r2dl4 ... SVE and water extraction following NAPL redistribution

         OUTPUT DATA AFTER (  70,  6)-2-TIME STEPS                                                    THE TIME IS   .36525E+03 DAYS
@@@
```

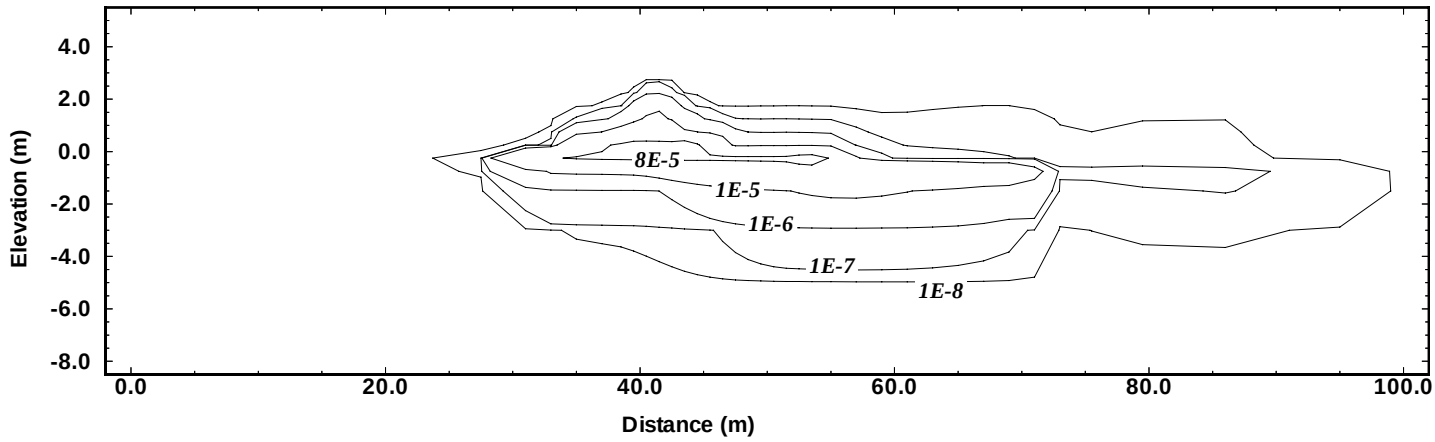


Figure 10.7.15. Contour plot of total VOC mass fraction in the aqueous phase at the end of the extraction period.

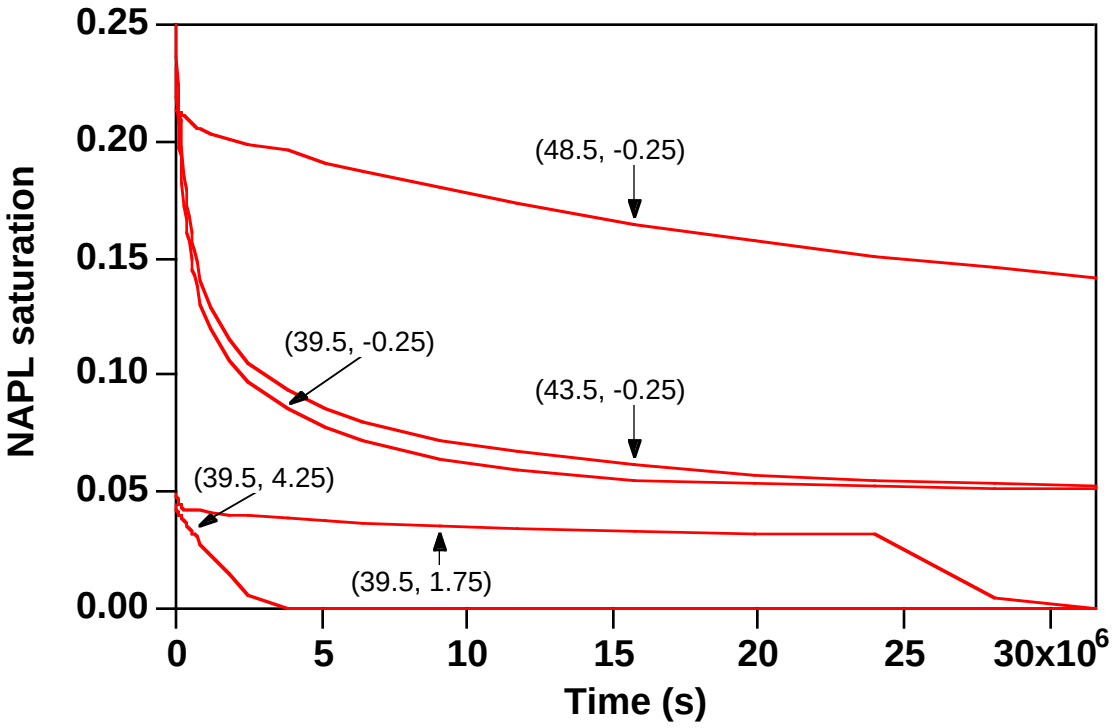


Figure 10.7.16. Evolution of NAPL saturation at selected locations, labeled with x, z-values.

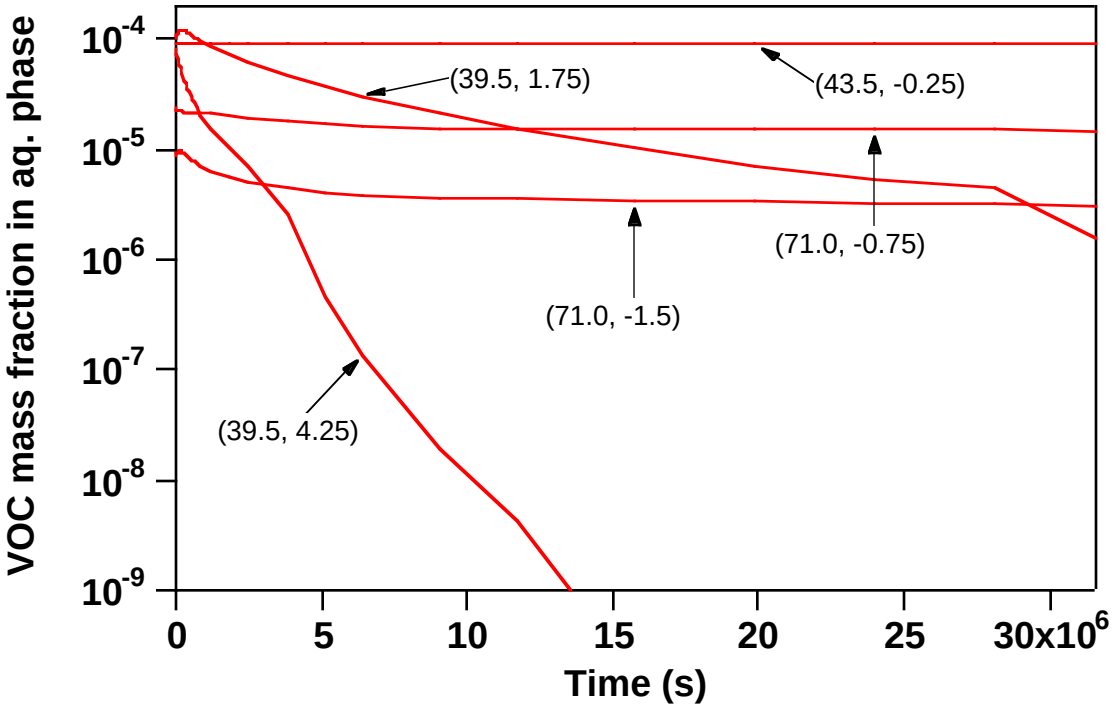


Figure 10.7.17. Evolution of VOC mass fractions in aqueous phase at selected locations, labeled with x, z-values.

11. Concluding Remarks

TMVOC is a versatile numerical simulator for multi-phase flows involving aqueous, non-aqueous, and gas phases, which may include several volatile organic compounds, along with water and a variety of non-condensible gases. All possible phase combinations in a water-air-NAPL system are treated, including single-phase gas, aqueous, NAPL; two-phase gas-aqueous, gas-NAPL, and aqueous-NAPL; and three-phase gas-aqueous-NAPL. TMVOC has capabilities for modeling flow and transport processes in variably saturated media at ambient conditions, as well as under non-isothermal conditions such as electric resistance heating or steamflooding. The code is written in standard Fortran77, is part of the TOUGH2 family of codes (Pruess et al., 1999), and maintains cross-compatibility with the T2VOC code (Falta et al., 1995).

The sample problems discussed in this report illustrate code features, and can serve as templates for users developing their own applications. Full documentation on the mathematical model used and the preparation of input data is provided in appendices. There is a tremendous variety of flow problems that can be tackled with TMVOC. The code was designed to be robust and be able to cope with difficult issues of phase change, phase partitioning of components, and compositional variation in fluid phases. Naturally, code performance will depend on process characteristics and parameter choices in specific problems. In some cases, sensitivites can be such that minor changes in problem parameters and gridding can have strong impacts on solution progress. For example, a sensitive situation arises when during a simulation run a grid block comes very close to one or two phase boundaries, such as a block in single-phase liquid conditions being very close to evolving gas and/or NAPL. This can cause severe time stepping limitations, especially when the grid block is in a very “dynamic” situation, i.e., subject to large inflows and outflows from neighboring blocks that nearly cancel each other out. In some cases very minor alterations in parameters and initial conditions can have strong impacts on time stepping and convergence. Code performance on numerically sensitive problems can also be different for different computing platforms with different numbers of significant digits and slightly different roundoff.

Acknowledgement

The TMVOC code is based on the PhD research of Adeyinka Adenekan. The authors are indebted to Stefan Finsterle and Chao Shan for their review and code testing, and for valuable suggestions. This work was supported, in part, by the U.S. Department of Energy through the Office of Basic Energy Sciences under Contract No. DE-AC03-76SF00098. Partial support was also provided by a grant from Aquater S.p.A. (ENI group) to the Lawrence Berkeley National Laboratory in the frame of the REPIS project sponsored by the ENI Research Fund.

References

Adenekan, A.E. Numerical Modeling of Multiphase Transport of Multicomponent Organic Contaminants and Heat in the Subsurface, PhD thesis, University of California at Berkeley, Berkeley, CA 94720, 1992.

Adenekan, A.E., T.W. Patzek and K. Pruess. Modeling of Multiphase Transport of Multicomponent Organic Contaminants and Heat in the Subsurface: Numerical Model Formulation, *Water Resour.Res.*, Vol. 29, No. 11, pp. 3727-3740, 1993.

Battistelli, A., C. Calore and K. Pruess. The Simulator TOUGH2/EWASG for Modeling Geothermal Reservoirs with Brines and Non-Condensible Gas, *Geothermics*, Vol. 26, No. 4, pp. 437 - 464, 1997.

Bird, R., W.E. Stewart and E.N. Lightfoot. *Transport Phenomena*, John Wiley & Sons, New York, NY, 1960.

Cass, A., G.S. Campbell and T.L. Jones. Enhancement of Thermal Water Vapor Diffusion in Soil. *Soil Sci. Soc. Am. J.,* Vol. 48, no. 1, pp. 25 - 32, 1984.

Coats, K.H. Geothermal Reservoir Modeling, paper SPE-6892, presented at the 52nd Annual Fall Technical Conference and Exhibition of the SPE, Denver, Colorado, October 1977.

Coats, K.H. and A.B. Ramesh. Effects of Grid Type and Difference Scheme on Pattern Steamflood Simulation Results, paper SPE-11079, presented at the 57th Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers, New Orleans, LA, September 1982.

Coats, K.H. and B.D. Smith. Dead-End Pore Volume and Dispersion in Porous Media, *Soc. Pet. Eng. J.*, 73-84, March 1964.

de Marsily, G. *Quantitative Hydrogeology*, Academic Press, Orlando, FL, 1986.

Duff, I. S. MA28—A Set of FORTRAN Subroutines for Sparse Unsymmetric Linear Equations, AERE Harwell Report R 8730, 1977.

Edwards, A.L. TRUMP: A Computer Program for Transient and Steady State Temperature Distributions in Multidimensional Systems, National Technical Information Service, National Bureau of Standards, Springfield, VA, 1972.

Falta, R.W., K. Pruess, I. Javandel and P.A. Witherspoon. Density - Driven Flow of Gas in the Unsaturated Zone Due to the Evaporation of Volatile Organic Compounds, *Water. Resour. Res.*, Vol. 25, No. 10, pp. 2159 - 2169, 1989.

Falta, R.W., K. Pruess, S. Finsterle, and A. Battistelli. T2VOC User's Guide, Lawrence Berkeley Laboratory Report LBL-36400, March 1995.

Faust, C.R. Transport of Immiscible Fluids Within and Below the Unsaturated Zone: A Numerical Model, *Water Resour. Res.*, Vol. 21, No. 4, pp. 587 - 596, 1985.

Graboski, M. S. and Daubert, T.E. A Modified Soave Equation of State for Phase Equilibrium Calculations 1. Hydrocarbon System, *Ind. Eng. Chem. Process Des. Dev.,* Vol. 17, pp. 443-448, 1978.

Hadgu, T., R.W. Zimmerman and G.S. Bodvarsson. Coupling of a Reservoir Simulator and a Wellbore Simulator for Geothermal Applications, *GRC Transactions,* Vol. 17, pp. 499 - 505, 1993.

Harvey, C. and S.M. Gorelick. Rate-limited Mass Transfer or Macrodispersion: Which Dominates Plume Evolution at the Macrodispersion Experiment (MADE) Site?, *Water Resour. Res.,* Vol. 36, No. 3, pp. 637 - 650, 2000.

Ho, C.K. Numerical Simulation of Multicomponent Evaporation and Gas-Phase Transport Using M2NOTS. Proceedings TOUGH Workshop '95, LBNL, Berkeley, CA, March 20-22, 1995.

Hoot W.F., A. Azarnoosh and J.J. McKetta, Jr. Solubility of Water in Hydrocarbons. *Pet. Refiner,* Vol. 36, pp. 255 - 256, 1957.

Hunt, J. R., N. Sitar and K. S. Udell. Nonaqueous Phase Liquid Transport and Cleanup, 2. Experimental Studies. *Water. Res. Res.*, 24 (8), 1259-1269, 1988.

International Association for the Properties of Steam. *Release on Dynamic Viscosity of Water Substance,* National Bureau of Standards, Washington, DC, 1975 (revised 1983).

International Formulation Committee. *A Formulation of the Thermodynamic Properties of Ordinary Water Substance,* IFC Secretariat, Düsseldorf, Germany, 1967.

Irvine, T.F. Jr and Liley, P.E. *Steam and Gas Tables with Computer Equations*. Academic Press Inc., Orlando, Florida, 185 pp, 1984.

Jury, W.A., W.F. Spencer and W.J. Farmer. Behavior Assessment Model for Trace Organics in Soil: I. Model Description, *J. Environ. Qual.,* Vol. 12, no. 4, pp. 558 - 564, 1983.

Karickhoff, S.W., D.S. Brown and T. A. Scott. Sorption of Hydrophobic Pollutants on Natural Sediments, *Water Resour. Res.*, Vol. 13, pp. 241 - 248, 1979.

Klinkenberg, L.J. The Permeability of Porous Media to Liquids and Gases, in *API Drilling and Production Practice,* pp. 200–213, 1941.

Kruger, P. and H.J. Ramey, Jr. Stimulation and Reservoir Engineering of Geothermal Resources, Stanford Geothermal Program Report SGR-TR-1, Stanford University, Stanford, CA, 1974.

Lam, S.T., A. Hunsbedt, P. Kruger and K. Pruess. Analysis of the Stanford Geothermal Reservoir Model Experiments Using the LBL Reservoir Simulator, *Geothermics*, 17 (4), 595–605, LBL-25957, 1988.

Leverett, M.C. Capillary Behavior in Porous Solids, *Trans. Soc. Pet. Eng. AIME*, 142, 152-169, 1941.

Mason, E.A. and A.P. Malinauskas. *Gas Transport in Porous Media: The Dusty Gas Model,* Elsevier, Amsterdam, The Netherlands, 1983.

McCain, W.D. Jr. *The Properties of Petroleum Fluids. 2nd edition,* PennWell Publishing Company, 548 p., 1990.

Meyer, C. A., R.B. McClintock, G.J. Silvestri and R.C. Spencer. *ASME Steam Tables,* The American Society of Mechanical Engineers, New York, U.S.A., 329 pp,, 1977.

Millington, R.J. and J.P. Quirk. Permeability of Porous Solids, *Trans. Faraday Soc.*, 57, 1200-1207, 1961.

Moridis, G. and K. Pruess. TOUGH Simulations of Updegraff's Set of Fluid and Heat Flow Problems, Lawrence Berkeley Laboratory Report LBL-32611, Berkeley, CA, November 1992.

Moridis, G. and K. Pruess. Flow and Transport Simulations Using T2CG1, a Package of Conjugate Gradient Solvers for the TOUGH2 Family of Codes, Lawrence Berkeley Laboratory Report LBL-36235, Lawrence Berkeley Laboratory, Berkeley, CA, 1995.

Moridis, G. and K. Pruess. T2SOLV: An Enhanced Package of Solvers for the TOUGH2 Family of Reservoir Simulation Codes, *Geothermics*, Vol. 27, No. 4, pp. 415 - 444, 1998.

Narasimhan, T.N. and P.A. Witherspoon. An Integrated Finite Difference Method for Analyzing Fluid Flow in Porous Media, *Water Resour. Res.*, Vol. 12, No. 1, pp. 57 – 64, 1976.

Parker, J.C., R.J. Lenhard and T. Kuppusamy. A Parametric Model for Constitutive Properties Governing Multiphase Flow in Porous Media, *Water Resour. Res.*, Viol. 23, No. 4, pp. 618 - 624, 1987.

Peaceman, D.W. *Fundamentals of Numerical Reservoir Simulation*, Elsevier, Amsterdam, The Netherlands, 1977.

Peaceman, D.W. Interpretation of Well-Block Pressures in Numerical Reservoir Simulation with Nonsquare Grid Blocks and Anisotropic Permeability, paper SPE-10528, presented at the Sixth SPE Symposium on Reservoir Simulation of the Society of Petroleum Engineers, New Orleans, LA, January 1982.

Peng, D.Y. and D.B. Robinson. A New Two-Constant Equation of State, *I.&E.C. Fundamentals,* Vol. 15, No. 1, pp. 59 - 64, 1976.

Prausnitz, J. M., R. N. Lichtenthaler, and E. G. de Azevedo. *Molecular Thermodynamics of Fluid-Phase Equilibria,* Prentice-Hall Inc., Englewood Cliffs, N. J., 1986.

Pritchett, J.W. and S.K. Garg. Determination of Effective Wellblock Radii for Numerical Reservoir Simulators, *Water Resour. Res.,* Vol. 16, No. 4, pp. 665 - 674, 1980.

Pruess, K. Heat Transfer in Fractured Geothermal Reservoirs with Boiling, *Water Resour. Res.,* Vol. 19, No. 1, pp. 201 - 208, 1983a.

Pruess, K. GMINC - A Mesh Generator for Flow Simulations in Fractured Reservoirs, Report No. LBL-15227, Lawrence Berkeley Laboratory, Berkeley, CA, 1983b.

Pruess, K. and G.S. Bodvarsson. A Seven-Point Finite Difference Method for Improved Grid Orientation Performance in Pattern Steam Floods. *Proceedings*, Seventh Society of Petroleum Engineers Symposium on Reservoir Simulation, pp. 175 - 184, San Francisco, CA, 1983.

Pruess, K., and T.N. Narasimhan. On Fluid Reserves and the Production of Superheated Steam from Fractured, Vapor-Dominated Geothermal Reservoirs, *J. Geophys. Res.*, 87 (B11), 9329-9339, 1982.

Pruess, K. and T.N. Narasimhan. A Practical Method for Modeling Fluid and Heat Flow in Fractured Porous Media, *Soc. Pet. Eng. J.*, Vol. 25, No. 1, pp. 14 - 26, February 1985.

Pruess, K., C. Oldenburg and G. Moridis. TOUGH2 User's Guide, Version 2.0, Lawrence Berkeley National Laboratory Report LBNL-43134, Berkeley, CA, November 1999.

Pruess, K., A. Simmons, Y.S. Wu and G. Moridis. TOUGH2 Software Qualification. Lawrence Berkeley National Laboratory Report LBL-38383, February 1996.

Redlich, O. and J.N.S. Kwong. On the Thermodynamics of Solutions. V - An Equation of State. Fugacities of Gaseous Solutions, *Chem. Reviews,* Vol. 44, pp. 233 - 244, 1949.

Reid, R.C., J.M. Prausnitz, and B.E. Poling. *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1987.

Schwarzenbach, R.P. and J. Westall. Transport of Non-polar Organic Compounds from Surface Water to Groundwater, Laboratory Sorption Studies, *Environ. Sci. Technol.*, Vol. 15, pp. 1360 - 1375, 1981.

Sleijpen, G.L.G. and D. Fokkema. BiCGSTAB(m) for Linear Equations Involving Unsymmetric Matrices with Complex Spectrum, *Electronic Transactions on Numerical Analysis*, Vol. 1, pp. 11 - 32, 1993.

Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State, *Chem. Eng. Sci.,* Vol. 27, No. 6, pp. 1197 - 1203, 1972.

Stone, H.L. Probability Model for Estimating Three-Phase Relative Permeability, *Trans. SPE of AIME*, 249, 214-218, 1970.

Thomas, G.W. *Principles of Hydrocarbon Reservoir Simulation*. International Human Resources Development Corporation, Boston, 1982.

van der Vorst, H.A. Bi-CGSTAB: A Fast and Smoothly Converging Variant of BiCG in the Presence of Rounding Errors, *SIAM J. Sci. Statist. Comput.*, Vol. 13, pp. 631 - 644, 1992.

van Velzen, D., R.L. Cardozo, and H. Langenkamp. A Liquid Viscosity-Temperature-Chemical Constitution Relation for Organic Compounds, *Ind. Eng. Chem. Fund.,* Vol. 11, No. 1, pp. 20 - 25, 1972.

Vargaftik, N.B. *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd Ed., John Wiley & Sons, New York, NY, 1975.

Vinsome, P.K.W. and J. Westerveld. A Simple Method for Predicting Cap and Base Rock Heat Losses in Thermal Reservoir Simulators, *J. Canadian Pet. Tech.*, Vol. 19, No. 3, pp. 87 – 90, July-September 1980.

Walker, W.R., J.D. Sabey, and D.R. Hampton. Studies of Heat Transfer and Water Migration in Soils, Final Report, Department of Agricultural and Chemical Engineering, Colorado State University, Fort Collins, CO, 80523, April 1981.

Warren, J.E. and P.J. Root. The Behavior of Naturally Fractured Reservoirs, *Soc. Pet. Eng. J., Transactions, AIME, 228*, 245-255, September 1963.

Webb, S.W. Gas-Phase Diffusion in Porous Media - Evaluation of an Advective-Dispersive Formulation and the Dusty Gas Model for Binary Mixtures, *J. Por. Media,* Vol. 1, No. 2, pp. 187 - 199, 1998.

Webb, S.W. and C.K. Ho. Review of Enhanced Vapor Diffusion in Porous Media, in: K. Pruess (ed.), Proceedings of the TOUGH Workshop '98, Lawrence Berkeley National Laboratory Report LBNL-41995, pp. 257 - 262, 1998a.

Webb, S.W. and C.K. Ho. Pore-Scale Modeling Using TOUGH2, in: K. Pruess (ed.), Proceedings of the TOUGH Workshop '98, Lawrence Berkeley National Laboratory Report LBNL-41995, pp. 288 - 293, 1998b.

Wilke, C.R. A Viscosity Equation for Gas Mixtures, *J. Chem. Phys.,* Vol. 18, No. 4, pp. 517 - 519, 1950.

Yaws, C.L., J.W. Miller, P.N. Shah, G.R. Schorr and P.M. Patel. Correlation Constants for Chemical Compounds, *Chem. Eng. Sci.,* Vol. 83, No. 24, pp. 153 - 162, 1976.

Appendix A. Mass and Energy Balances

The basic mass- and energy-balance equations solved by TMVOC or any other member of the TOUGH2 family of codes can be written in the general form

$$\frac{d}{dt}\int_{V_n} M^\kappa \, dV_n = \int_{\Gamma_n} \mathbf{F}^\kappa \bullet \mathbf{n} \, d\Gamma_n + \int_{V_n} q^\kappa dV_n \qquad (A.1)$$

The integration is over an arbitrary subdomain V_n of the flow system under study, which is bounded by the closed surface Γ_n. The quantity M appearing in the accumulation term (left hand side) represents mass or energy per volume, with $\kappa = 1, ..., NK$ labeling the mass components (water, NCGs, volatile organic chemicals), and $\kappa = NK + 1$ the heat "component." **F** denotes mass or heat flux (see below), and q denotes sinks and sources. **n** is a normal vector on surface element $d\Gamma_n$, pointing inward into V_n.

The mass accumulation term for the water and NCG components is

$$M^\kappa = \phi \sum_\beta S_\beta \rho_\beta x_\beta^\kappa \qquad (A.2)$$

The total mass of component κ is obtained by summing over the fluid phases β (= liquid, gas, NAPL). ϕ is porosity, S_β is the saturation of phase β (i.e., the fraction of pore volume occupied by phase β), ρ_β is the density of phase β, and x_β^κ is the mole fraction of component κ present in phase β. In TMVOC all mass densities are expressed in molar units (gram-moles per m^3); the composition of fluid phases is then expressed in terms of mole fractions of the different components. (Other members of the TOUGH2 family of codes use mass units and mass fractions. The governing equations have the same form, regardless of whether mass or molar units are used.) For the VOCs a more general form of the mass accumulation term is used that includes equilibrium sorption on the solid grains.

$$M^\kappa = \phi \sum_\beta S_\beta \rho_\beta x_\beta^\kappa + (1-\phi)\rho_R \rho_w x_w^\kappa K_d \qquad (A.3)$$

Here, ρ_R is the density of the rock grains, ρ_w is the density of the aqueous phase, x_w^κ is the mole fraction of VOC component κ in the aqueous phase, and K_d is the aqueous phase distribution coefficient (de Marsily, 1986, p. 256). Similarly, the heat accumulation term in a multiphase system is

$$M^{NK+1} = (1-\phi)\rho_R C_R T + \phi \sum_\beta S_\beta \rho_\beta u_\beta \qquad (A.4)$$

where C_R is specific heat of the rock, T is temperature, and u_β is specific internal energy in phase β (in TMVOC, specific internal energy and enthalpy are expressed in units of J/mole).

Advective mass flux is a sum over phases,

$$\mathbf{F}^\kappa\Big|_{adv} = \sum_\beta x_\beta^\kappa \mathbf{F}_\beta \qquad (A.5)$$

and indiv.a multiphase version of Darcy's law:

$$\mathbf{F}_\beta = \rho_\beta \mathbf{u}_\beta = -k \frac{k_{r\beta}\rho_\beta}{\mu_\beta}(\nabla P_\beta - \rho_\beta \mathbf{g}) \qquad (A.6)$$

Here $\mathbf{u}_\beta$ is the Darcy velocity (volume flux) in phase β, k is absolute permeability, $k_{r\beta}$ is relative permeability to phase β, μ_β is viscosity, and

$$P_\beta = P + P_{c\beta} \qquad (A.7)$$

is the fluid pressure in phase β, which is the sum of the pressure P of a reference phase (usually taken to be the gas phase), and the capillary pressure $P_{c\beta}$ (≤ 0). $\mathbf{g}$ is the vector of gravitational acceleration.

Heat flux includes conductive and convective components

$$\mathbf{F}^{NK+1} = -K\nabla T + \sum_\beta h_\beta \mathbf{F}_\beta \qquad (A.8)$$

where K is thermal conductivity, and h_β is specific enthalpy in phase β. Radiative heat transfer according to the Stefan-Boltzmann law can also be modeled (see Eq. E.2).

Absolute permeability of the gas phase increases at low pressures according to the relation given by Klinkenberg (1941)

$$k = k_\infty \left(1 + \frac{b}{P}\right) \qquad (A.9)$$

where k_∞ is the permeability at "infinite" pressure, and b is the Klinkenberg parameter. In addition to Darcy flow, mass transport can also occur by diffusion. The diffusive flux of component κ in phase β is given by (see Appendix D)

$$\mathbf{f}_\beta^\kappa = -\phi \tau_0 \tau_\beta \rho_\beta d_\beta^\kappa \nabla x_\beta^\kappa \tag{A.10}$$

By applying Gauss' divergence theorem, Eq. (A.1) can be converted into the following PDE

$$\frac{\partial M^\kappa}{\partial t} = -\operatorname{div} \mathbf{F}^\kappa + q^\kappa \tag{A.11}$$

which is the form commonly used as the starting point for deriving finite difference or finite element discretization approaches.

Appendix B. Space and Time Discretization

The continuum equations (A.1) are discretized in space using the integral finite difference (IFD) method (Edwards, 1972; Narasimhan and Witherspoon, 1976). Introducing appropriate volume averages, we have

$$\int_{V_n} M \, dV \quad = \quad V_n \, M_n \tag{B.1}$$

where M is a volume-normalized extensive quantity, and M_n is the average value of M over V_n. Surface integrals are approximated as a discrete sum of averages over surface segments A_{nm}:

$$\int_{\Gamma_n} \mathbf{F}^{\kappa} \bullet \mathbf{n} \, d\Gamma \quad = \quad \sum_m A_{nm} \, F_{nm} \tag{B.2}$$

Here F_{nm} is the average value of the (inward) normal component of **F** over the surface segment A_{nm} between volume elements V_n and V_m. The discretization approach used in the integral finite difference method and the definition of the geometric parameters are illustrated in Fig. B.1.

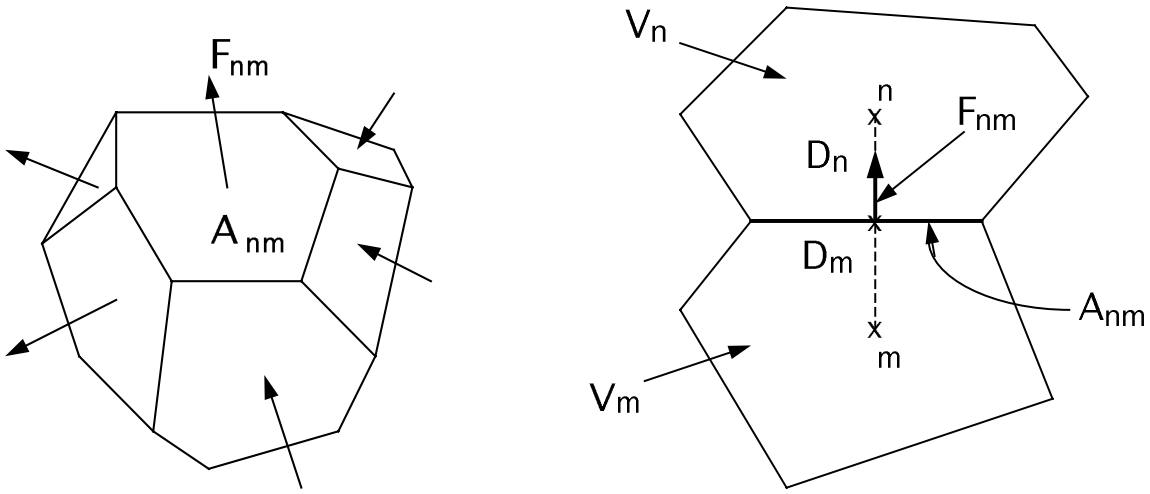


Figure B.1. Space discretization and geometry data in the integral finite difference method.

The discretized flux is expressed in terms of averages over parameters for elements V_n and V_m. For the basic Darcy flux term, Eq. (A.6), we have

$$F_{\beta,nm} = -k_{nm}\left[\frac{k_{r\beta}\,\rho_\beta}{\mu_\beta}\right]_{nm}\left[\frac{P_{\beta,n}-P_{\beta,m}}{D_{nm}}-\rho_{\beta,nm}\,g_{nm}\right] \tag{B.3}$$

where the subscripts (nm) denote a suitable averaging at the interface between grid blocks n and m (interpolation, harmonic weighting, upstream weighting). $D_{nm} = D_n + D_m$ is the distance between the nodal points n and m, and g_{nm} is the component of gravitational acceleration in the direction from m to n. Discretization of diffusive fluxes raises some subtle issues and is discussed separately in Appendix D.

Substituting Eqs. (B.l) and (B.2) into the governing Eq. (A.1), a set of first-order ordinary differential equations in time is obtained.

$$\frac{dM_n^\kappa}{dt} = \frac{1}{V_n}\sum_m A_{nm}\,F_{nm}^\kappa + q_n^\kappa \tag{B.4}$$

Time is discretized as a first-order finite difference, and the flux and sink and source terms on the right-hand side of Eq. (B.4) are evaluated at the new time level, $t^{k+l} = t^k + \Delta t$, to obtain the numerical stability needed for an efficient calculation of multiphase flow. This treatment of flux terms is known as "fully implicit," because the fluxes are expressed in terms of the unknown thermodynamic parameters at time level t^{k+l}, so that these unknowns are only implicitly defined in the resulting equations (see, e.g., Peaceman, 1977). The time discretization results in the following set of coupled non-linear, algebraic equations

$$\begin{aligned} R_n^{\kappa,k+1} &= M_n^{\kappa,k+1} - M_n^{\kappa,k} - \frac{\Delta t}{V_n}\left\{\sum_m A_{nm}\,F_{nm}^{\kappa,k+1} + V_n\,q_n^{\kappa,k+1}\right\} \\ &= 0 \end{aligned} \tag{B.5}$$

where we have introduced residuals $R_n^{\kappa,k+1}$. For each volume element (grid block) V_n, there are NEQ equations (κ = 1, 2, ..., NEQ; usually, NEQ = NK + 1), so that for a flow system with NEL grid blocks (B.5) represents a total of NEL x NEQ coupled non-linear equations. The unknowns are the NEL x NEQ independent primary variables $\{x_i;\ i = 1, ..., NEL \times NEQ\}$ which completely define the state of the flow system at time level t^{k+l}. These equations are solved by Newton/Raphson iteration, which is implemented as follows. We introduce an iteration index p and

expand the residuals $R_n^{\kappa,k+1}$ in Eq. (B.5) at iteration step p + 1 in a Taylor series in terms of those at index p.

$$R_n^{\kappa,k+1}\left(x_{i,p+1}\right) \;=\; R_n^{\kappa,k+1}\left(x_{i,p}\right) + \sum_i \left.\frac{\partial R_n^{\kappa,k+1}}{\partial x_i}\right|_p \left(x_{i,p+1} - x_{i,p}\right) + \ldots \;=\; 0 \qquad \text{(B.6)}$$

Retaining only terms up to first order, we obtain a set of NEL x NEQ linear equations for the increments $(x_{i,p+1} - x_{i,p})$:

$$-\sum_i \left.\frac{\partial R_n^{\kappa,k+1}}{\partial x_i}\right|_p \left(x_{i,p+1} - x_{i,p}\right) \;=\; R_n^{\kappa,k+1}\left(x_{i,p}\right) \qquad \text{(B.7)}$$

All terms $\partial R_n/\partial x_i$ in the Jacobian matrix are evaluated by numerical differentiation. Eq. (B.7) is solved by sparse direct matrix methods (Duff, 1977) or iteratively by means of preconditioned conjugate gradients (Moridis and Pruess, 1995, 1998). Iteration is continued until the residuals $R_n^{\kappa,k+1}$ are reduced below a preset convergence tolerance.

$$\left|\frac{R_{n,p+1}^{\kappa,k+1}}{M_{n,p+1}^{\kappa,k+1}}\right| \;\le\; \varepsilon_1 \qquad \text{(B.8)}$$

The default (relative) convergence criterion is $\varepsilon_1 = 10^{-5}$ (TMVOC input parameter RE1). Eq. (B.8) may be difficult (and unnecessary) to satisfy for mass components that are present in small or trace amounts, as may often be the case for VOCs in contamination problems. To address this issue, a second parameter ε_2 is introduced that allows to relax convergence requirements for components that are present in small quantities. When the accumulation terms are smaller than ε_2 (TMVOC input parameter RE2, default $\varepsilon_2 = 1$), an absolute convergence criterion is imposed.

$$|R_n^{\kappa,k+1}| \le \varepsilon_1 \bullet \varepsilon_2 \qquad \text{(B.9)}$$

Convergence is usually attained in 3 - 4 iterations. If convergence cannot be achieved within a certain number of iterations (default 8), the time step size Δt is reduced and a new iteration process is started.

It is appropriate to add some comments about our space discretization technique. The entire geometric information of the space discretization in Eq. (B.5) is provided in the form of a list of grid block volumes V_n, interface areas A_{nm}, nodal distances D_{nm} and components g_{nm} of gravitational acceleration along nodal lines. There is no reference whatsoever to a global system of coordinates, or to the dimensionality of a particular flow problem. The discretized equations are in fact valid for arbitrary irregular discretizations in one, two or three dimensions, and for porous as well as for fractured media. This flexibility should be used with caution, however, because the accuracy of solutions depends upon the accuracy with which the various interface parameters in equations such as (B.3) can be expressed in terms of average conditions in grid blocks. A general requirement is that there exists approximate thermodynamic equilibrium in (almost) all grid blocks at (almost) all times (Pruess and Narasimhan, 1985). For systems of regular grid blocks referenced to global coordinates (such as r - z, x - y - z), Eq. (B.5) is identical to a conventional finite difference formulation (e.g., Peaceman, 1977; Moridis and Pruess, 1992).

Appendix C. Description of Flow in Fractured Media

Figure C.1 illustrates the classical double-porosity concept for modeling flow in fractured-porous media as developed by Warren and Root (1963). Matrix blocks of low permeability are embedded in a network of interconnected fractures. Global flow in the reservoir occurs only through the fracture system, which is described as an effective porous continuum. Rock matrix and fractures may exchange fluid (or heat) locally by means of "interporosity flow," which is driven by the difference in pressures (or temperatures) between matrix and fractures. Warren and Root approximated the interporosity flow as being quasi-steady, with rate of matrix-fracture interflow proportional to the difference in (local) average pressures.

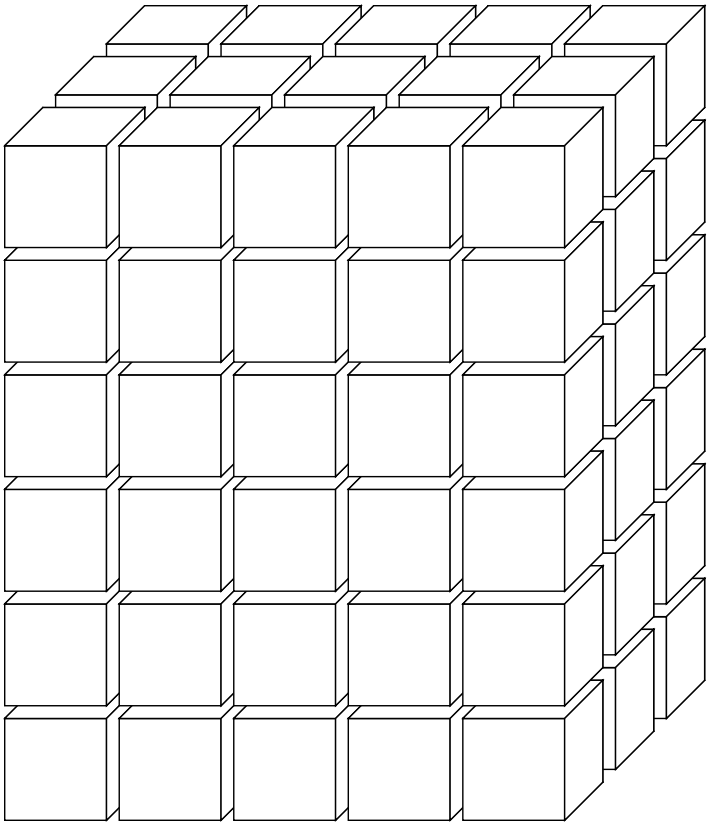


Figure C.1. Idealized double porosity model of a fractured porous medium.

The quasi-steady approximation is applicable to isothermal single-phase flow of fluids with small compressibility, where pressure diffusivities are large, so that pressure changes in the fractures penetrate quickly all the way into the matrix blocks. However, for multiphase flows, or coupled fluid and heat flows, the transient periods for interporosity flow can be very long (tens of years). In order to accurately describe such flows it is necessary to resolve the driving pressure, temperature, and mass fraction gradients at the matrix/fracture interface. In the method of "multiple

interacting continua" (MINC; Pruess and Narasimhan, 1982, 1985), resolution of these gradients is achieved by appropriate subgridding of the matrix blocks, as shown in Fig. C.2. The MINC concept is based on the notion that changes in fluid pressures, temperatures, phase compositions, etc. due to the presence of sinks and sources (production and injection wells) will propagate rapidly through the fracture system, while invading the tight matrix blocks only slowly. Therefore, changes in matrix conditions will (locally) be controlled by the distance from the fractures. Fluid and heat flow from the fractures into the matrix blocks, or from the matrix blocks into the fractures, can then be modeled by means of one-dimensional strings of nested grid blocks, as shown in Fig. C.2.

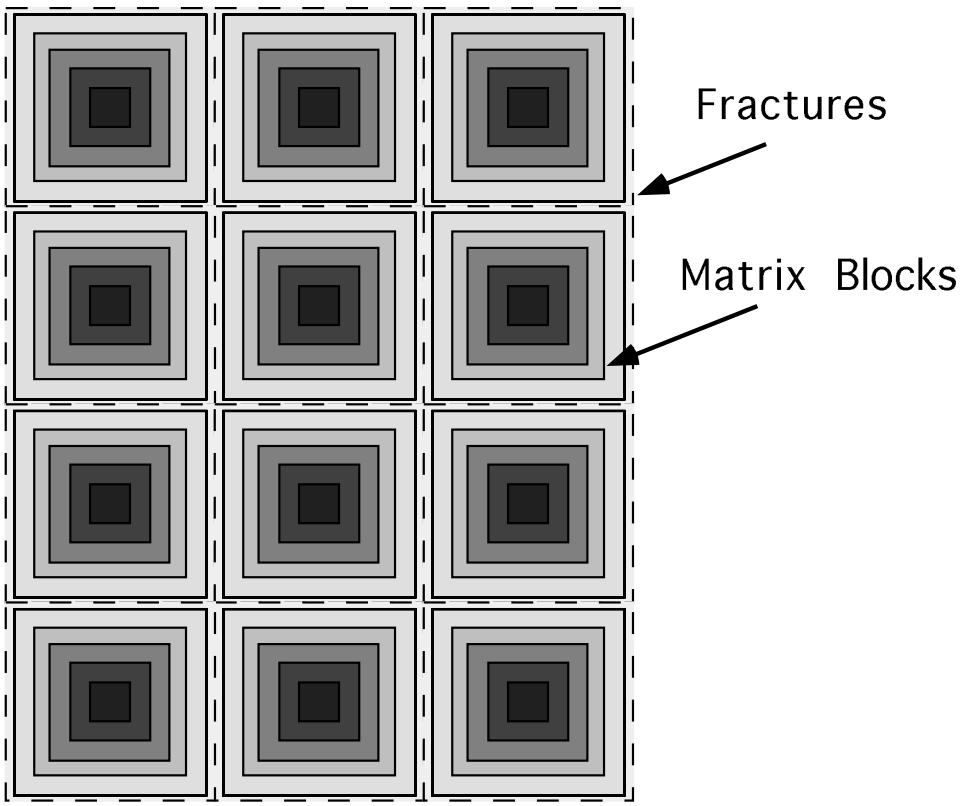


Figure C.2. Subgridding in the method of "multiple interacting continua" (MINC).

In general it is not necessary to explicitly consider subgrids in all of the matrix blocks separately. Within a certain reservoir subdomain (corresponding to a finite difference grid block), all fractures will be lumped into continuum # 1, all matrix material within a certain distance from the fractures will be lumped into continuum # 2, matrix material at larger distance becomes continuum # 3, and so on. Quantitatively, the subgridding is specified by means of a set of volume fractions VOL(j), j = 1, ..., J, into which the primary porous medium grid blocks are partitioned. The MINC-process in the MESHMAKER module of TMVOC operates on the element and connection data of

a porous medium mesh to calculate, for given data on volume fractions, the volumes, interface areas, and nodal distances for a secondary fractured medium mesh. The information on fracturing (spacing, number of sets, shape of matrix blocks) required for this is provided by a "proximity function" PROX(x) which expresses, for a given reservoir domain V_o, the total fraction of matrix material within a distance x from the fractures. If only two continua are specified (one for fractures, one for matrix), the MINC approach reduces to the conventional double-porosity method. Full details are given in a separate report (Pruess, 1983b).

The MINC-method as implemented in the MESHMaker module can also describe global matrix-matrix flow. Fig. C.3 shows the most general approach, often referred to as "dual permeability," in which global flow occurs in both fracture and matrix continua. It is also possible to permit matrix-matrix flow only in the vertical direction. For any given fractured reservoir flow problem, selection of the most appropriate gridding scheme must be based on a careful consideration of the physical and geometric conditions of flow. The MINC approach is not applicable to systems in which fracturing is so sparse that the fractures cannot be approximated as a continuum.

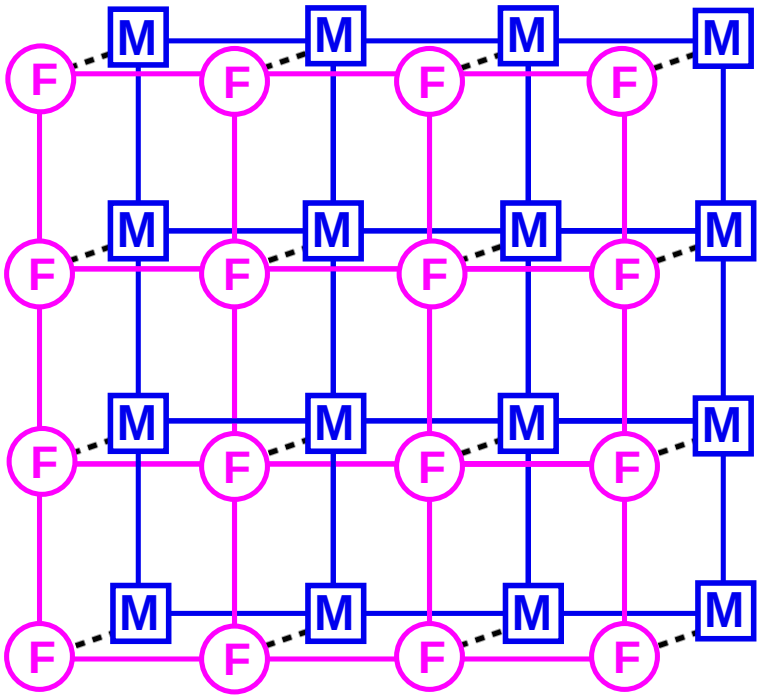


Figure C.3. Flow connections in the "dual permeability" model. Global flow occurs between both fracture (F) and matrix (M) grid blocks. In addition there is F-M interporosity flow.

Appendix D. Multiphase Diffusion

D.1 General Considerations

Molecular diffusion plays a minor role in many subsurface flow processes, but may become a significant and even dominant mechanism for mass transport when advective velocities are small. Diffusive flux is usually written as being proportional to the gradient in the concentration of the diffusing component (Fick's law)

$$\mathbf{f} = -d\nabla C \tag{D.1}$$

where d is an effective diffusivity, which in general will depend on properties of the diffusing component, the pore fluid, and the porous medium. The concentration variable C may be chosen in a number of different ways (mass per unit volume, moles per unit volume, mass or mole fraction, etc.; Bird et al., 1960; de Marsily, 1986).

The basic Fick's law Eq. D.1 works well for diffusion of tracer solutes that are present at low concentrations in a single phase aqueous solution at rest with respect to the porous medium. However, many subtleties and complications arise when multiple components diffuse in a multiphase flow system. Effective diffusivities in general may depend on all concentration variables, leading to non-linear behavior especially when some components are present in significant (non-tracer) concentrations. Additional nonlinear effects arise from the dependence of tortuosity on phase saturations, and from coupling between advective and diffusive transport. For gases the Fickian model has serious limitations even at low concentrations, which prompted the development of the "dusty gas" model that entails a strong coupling between advective and diffusive transport (Mason and Malinauskas, 1983; Webb, 1998), and accounts for molecular streaming effects (Knudsen diffusion) that become very important when the mean free path of gas molecules is comparable to pore sizes. Further complications arise for components that are both soluble and volatile, in which case diffusion in aqueous and gaseous phases may be strongly coupled via phase partitioning effects. An extreme case is the well-known enhancement of vapor diffusion in partially saturated media, that is attributed to pore-level phase change effects (Cass et al., 1984; Webb and Ho, 1998a, b).

D.2 Formulation Used in TMVOC

Because of the difficulties mentioned above, it is not possible to formulate a model for multiphase diffusion that would be accurate under all circumstances. We have used a pragmatic approach in which diffusive flux of component κ in phase β (= gas, water, oil) is written as

$$\mathbf{f}_\beta^\kappa = -\phi \tau_0 \tau_\beta \rho_\beta d_\beta^\kappa \nabla x_\beta^\kappa \qquad (D.2)$$

where ϕ is porosity, $\tau_0\tau_\beta$ is the tortuosity which includes a porous medium dependent factor τ_0 and a coefficient that depends on phase saturation S_β, $\tau_\beta = \tau_\beta(S_\beta)$, ρ_β is density, d_β^κ is the diffusion coefficient of component κ in bulk fluid phase β, and x_β^κ is the mole fraction of component κ in phase β. For later developments it will be useful to define a single diffusion strength factor which combines all material constants and tortuosity factors into a single effective multiphase diffusion coefficient, as follows.

$$\Sigma_\beta^\kappa = \phi \tau_0 \tau_\beta \rho_\beta d_\beta^\kappa \qquad (D.3)$$

For general three-phase conditions, the total diffusive flux is then given by

$$\mathbf{f}^\kappa = -\Sigma_g^\kappa \nabla x_g^\kappa - \Sigma_w^\kappa \nabla x_w^\kappa - \Sigma_o^\kappa \nabla x_o^\kappa \qquad (D.4)$$

Here we use the subscript "o" for the NAPL (oil) phase rather than n, to avoid confusion with the customary use of n for numbering grid blocks, see below.

The saturation dependence of tortuosity is not well known at present. For soils the Millington and Quirk (1961) model has frequently been used (Jury et al., 1983; Falta et al., 1989)

$$\tau_0 \tau_\beta = \phi^{1/3} S_\beta^{10/3} \qquad (D.5)$$

which yields non-zero tortuosity coefficients as long as phase saturation is non-zero. It stands to reason that diffusive flux should vanish when a phase becomes discontinuous at low saturations, suggesting that saturation-dependent tortuosity should be related to relative permeability; e.g. $\tau_\beta(S_\beta) \approx k_{r\beta}(S_\beta)$. However, for components that partition between liquid and gas phases more complex behavior may be expected. For example, consider the case of a volatile and water-soluble compound diffusing under conditions of low gas saturation where the gas phase is discontinuous. In this case we have $k_{rg}(S_g) = 0$ (because $S_g < S_{gr}$), and $k_{rw}(S_w = 1\text{-}S_g) < 1$, so that a model equating saturation-dependent tortuosity to relative permeability would predict weaker diffusion than in single-phase liquid conditions. For compounds with "significant" volatility this would be unrealistic, as diffusion through isolated gas pockets would tend to enhance overall diffusion relative to single-phase liquid conditions.

D.3 Space Discretization

Space discretization of diffusive flux in multiphase conditions raises some subtle issues. A finite difference formulation for total diffusive flux, Eq. (D.4), may be written as

$$\left(f^{\kappa}\right)_{nm} = -\left(\Sigma_g^{\kappa}\right)_{nm} \frac{\left(x_g^{\kappa}\right)_m - \left(x_g^{\kappa}\right)_n}{D_{nm}} - \left(\Sigma_w^{\kappa}\right)_{nm} \frac{\left(x_w^{\kappa}\right)_m - \left(x_w^{\kappa}\right)_n}{D_{nm}} - \left(\Sigma_o^{\kappa}\right)_{nm} \frac{\left(x_o^{\kappa}\right)_m - \left(x_o^{\kappa}\right)_n}{D_{nm}} \quad (D.6)$$

This expression involves the as yet unknown diffusive strength coefficients $(\Sigma_g^{\kappa})_{nm}$, $(\Sigma_w^{\kappa})_{nm}$ and $(\Sigma_o^{\kappa})_{nm}$ at the interface, which must be expressed in terms of the strength coefficients in the participating grid blocks. Invoking conservation of diffusive flux across the interface between two grid blocks leads in the usual way to the requirement of harmonic weighting of the diffusive strength coefficients. However, such weighting may in general not be applied separately to the diffusive fluxes in gas and liquid phases, because these may be strongly coupled by phase partitioning effects. This can be seen by considering the extreme case of diffusion of a water-soluble and volatile compound from a grid block in single-phase gas conditions to an adjacent grid block which is in single-phase liquid conditions. Harmonic weighting applied separately to liquid and gas diffusive fluxes would result in either of them being zero, because for each phase effective diffusivity is zero on one side of the interface. Thus total diffusive flux would vanish in this case, which is unphysical. In reality, tracer would diffuse through the gas phase to the gas-liquid interface, would establish a certain mass fraction in the aqueous phase by dissolution, and would then proceed to diffuse away from the interface through the aqueous phase. Similar arguments can be made in the less extreme situation where liquid saturation changes from a large to a small value rather than from 1 to 0, as may be the case in the capillary fringe, during infiltration events, or at fracture-matrix interfaces in variably saturated media.

TMVOC features a fully coupled approach in which the space-discretized version Eq. (D.6) of the total multiphase diffusive flux Eq. (D.4) is re-written in terms of an effective multiphase diffusive strength coefficient and a single mole fraction gradient. Choosing the water phase mole fraction for this we have

$$\left(f^{\kappa}\right)_{nm} = -\left\{\Sigma_w^{\kappa} + \Sigma_g^{\kappa} \frac{\left(x_g^{\kappa}\right)_m - \left(x_g^{\kappa}\right)_n}{\left(x_w^{\kappa}\right)_m - \left(x_w^{\kappa}\right)_n} + \Sigma_o^{\kappa} \frac{\left(x_o^{\kappa}\right)_m - \left(x_o^{\kappa}\right)_n}{\left(x_w^{\kappa}\right)_m - \left(x_w^{\kappa}\right)_n}\right\}_{nm} \frac{\left(x_w^{\kappa}\right)_m - \left(x_w^{\kappa}\right)_n}{D_{nm}} \quad (D.7)$$

where the gas and oil phase mole fraction gradients have been absorbed into the effective diffusive strength term (in braces). As is well known, flux conservation at the interface then leads to the

requirement of harmonic weighting for the full effective strength coefficient. In order to be able to apply this scheme to the general case where not all phases may be present on both sides of the interface, we always define the water phase mole fractions in all grid blocks, regardless of whether water phase is present or not. Mole fractions are assigned in such a way as to be consistent with what would be present in an evolving water phase. This procedure is applicable to all possible phase combinations, including the extreme case where conditions at the interface change from single phase gas to single phase oil. Note that, if the diffusing tracer exists in just a single phase, harmonic weighting of the strength coefficient in Eq. (D.7) will reduce to harmonic weighting of either Σ_g^κ, Σ_w^κ or Σ_o^κ.

The simpler scheme of separate harmonic weighting for individual phase diffusive fluxes is retained as an option, see below.

D.4 User Options

The treatment of multiphase diffusion requires parameter specifications in several different data blocks. In order to engage diffusion, the user must set the number of secondary parameters NB = 8 in data block MULTI; the alternative value NB = 6 will give a "no diffusion" calculation. Diffusivities are input through a new data block DIFFU.

Diffusion coefficients for gases depend on pressure and temperature as (Vargaftik, 1975; Walker et al., 1981)

$$d_\beta^\kappa(P,T) \;=\; d_\beta^\kappa(P_0,T_0)\,\frac{P_0}{P}\left[\frac{T+273.15}{273.15}\right]^\theta \qquad (D.8)$$

At standard conditions of P_0 = 1 atm ≡ 1.01325 bar, T_0 = 0 °C, the diffusion coefficient for vapor-air mixtures has a value of 2.13 x 10^{-5} m^2/s; parameter θ for the temperature dependence is 1.80. TMVOC can model a temperature dependence of gas phase diffusion coefficients according to Eq. (D.8) by specifying parameter θ = TEXP in the first record of data block PARAM (see p. 158). Presently there are no provisions for inputting different values for the parameter θ of temperature dependence for different gas phase components. Aqueous and NAPL phase diffusion coefficients are taken as constants, with no provisions for temperature dependence of these parameters.

Tortuosity effects have a porous medium-dependent part τ_0 and a saturation-dependent part τ_β, see Eq. (D.2). The following three alternative formulations are available.

1. Relative permeability model.
   For domains for which a tortuosity parameter τ_0 = TORTX $\neq$ 0 is specified in data block ROCKS, tortuosity will be taken as $\tau_0\tau_\beta(S_\beta) = \tau_0 k_{r\beta}(S_\beta)$.
2. Millington-Quirk model.
   For domains in which TORTX = 0, the Millington-Quirk model as given in Eq. (D.5) will be used.
3. Constant diffusivity.
   When diffusivities d_β^κ are specified as negative numbers, $\tau_0\tau_\beta = S_\beta$ will be used. Diffusivities will be taken to be the absolute values of the user inputs.

Alternative 3 corresponds to the formulation for gas diffusion in earlier versions of TOUGH2. In the absence of phase partitioning and adsorptive effects, it amounts to effective diffusivity being approximately equal to d_β^κ, independent of saturation. This can be seen by noting that the accumulation term in the phase β contribution to the mass balance equation for component κ is given by $\phi S_\beta \rho_\beta x_\beta^\kappa$, approximately canceling out the $\phi S_\beta \rho_\beta$ coefficient in the diffusive flux.

A crude (saturation-independent) enhancement of vapor diffusion can be chosen by specifying a suitable value, typically of order 1, for the parameter group $B = \phi\tau_0\tau_\beta$. This is to be entered as parameter BE in the first record in data block PARAM (see p. 158).

As had been discussed above, two alternative discretization schemes for diffusion are implemented in TMVOC. The default option is selected for MOP(24) = 0 and applies harmonic weighting to the full multiphase effective diffusion strength (see Eq. D.7). This includes contributions from gas, water, and oil phases, accounts for coupling of diffusion with phase partitioning effects, and can cope with the most general case of diffusion across a phase boundary. As an alternative, by setting MOP(24) = 1, harmonic weighting can be performed separately for the diffusive fluxes in gas, water, and oil phases.

Appendix E. TMVOC Input Formats

This appendix gives a complete reference for TMVOC input data. Data formats are identical to TOUGH2, Version 2.0, except for (1) the presence of new data blocks CHEMP and NCGAS with property data for the organic chemicals and non-condensible gases, respectively, and (2) slight differences in the formats for initial condition data. Input data for the MESHMAKER module are discussed in Appendix F.

TMVOC input data are organized in fixed-format blocks that are marked by keywords. Many of the data blocks may have variable length, some are optional. The main problem size-dependent data may be supplied by means of separate disk files rather than through the input file. Geometry data (computational grid) may be internally generated, or supplied through data blocks ELEME and CONNE, or provided by means of a file called MESH with data formats identical to blocks ELEME and CONNE. Initial conditions are supplied through data block INCON (and/or INDOM, PARAM.4-5) or through a disk file called INCON. Sink and source data are read from a data block GENER or from a disk file GENER.

The ordering of the data blocks is generally flexible; however, data block MULTI must precede data blocks PARAM, INDOM, and INCON. Block ELEME must precede CONNE.

TITLE — is the first record of the input file, containing a header of up to 80 characters, to be printed on output. This can be used to identify a problem. If no title is desired, leave this record blank.

MESHM — introduces parameters for internal mesh generation and processing. The MESHMaker input has a modular structure which is organized by keywords. Detailed instructions for preparing MESHMaker input are given in Appendix F.

Record MESHM.1

Format(A5)
WORD

WORD — enter one of several keywords, such as RZ2D, RZ2DL, XYZ, MINC, to generate different kinds of computational meshes.

Record MESHM.2 — A blank record closes the MESHM data block.

ENDFI — is a keyword that can be used to close a TMVOC input file when no flow simulation is desired. This will often be used for a mesh generation run when some hand-editing of the mesh will be needed before the actual flow simulation.

ROCKS introduces material parameters for up to 27 different reservoir domains.

Record ROCKS.1

Format (A5, I5, 7E10.4)
MAT, NAD, DROK, POR, (PER (I), I = 1,3), CWET, SPHT

MAT material name (rock type).

NAD if zero or negative, defaults will take effect for a number of parameters (see below);

≥1: will read another data record to override defaults.

≥2: will read two more records with domain-specific parameters for relative permeability and capillary pressure functions.

DROK rock grain density (kg/m^3)

POR default porosity (void fraction) for all elements belonging to domain "MAT" for which no other porosity has been specified in block INCON. Option "START" is necessary for using default porosity.

PER(I), I = 1,3 absolute permeabilities along the three principal axes, as specified by ISOT in block CONNE.

CWET formation heat conductivity under fully liquid-saturated conditions (W/m °C).

SPHT rock grain specific heat (J/kg °C). Domains with SPHT > 10^4 J/kg ° C will not be included in global material balances. This provision is useful for boundary nodes, which are given very large volumes so that their thermodynamic state remains constant. Because of the large volume, inclusion of such nodes in global material balances would make the balances useless.

Record ROCKS.1.1 (optional, NAD ≥ 1 only)

Format (7E10.4)
COM, EXPAN, CDRY, TORTX, GK, FOCM

COM pore compressiblity (Pa^{-1}), $(1/\phi)(\partial\phi/\partial P)_T$ (default is 0).

EXPAN pore expansivity (1/ °C), $(1/\phi)(\partial\phi/\partial T)_P$ (default is 0).

CDRY formation heat conductivity under desaturated conditions (W/m °C), (default is CWET).

TORTX tortuosity factor for binary diffusion. If TORTX = 0, a porosity and saturation-dependent tortuosity will be calculated internally from the Millington and Quirk (1961) model, Eq. (D.5).

GK Klinkenberg parameter b (Pa^{-1}) for enhancing gas phase permeability according to the relationship $k_{gas} = k_{liq} * (1 + b/P)$.

FOCM fraction of organic carbon present in domain; used for calculating amount of VOC adsorbed.

Record ROCKS.1.2 (optional, NAD ≥ 2 only)

Format (I5, 5X,7E10.4)
IRP, (RP(I), I= 1,7)

IRP integer parameter to choose type of relative permeability function (see Appendix G).

RP(I), I = 1, ..., 7 parameters for relative permeability function (Appendix G).

Record ROCKS.1.3 (optional, NAD ≥ 2 only)

Format (I5, 5X,7E10.4)
ICP, (CP(I), I = 1,7)

ICP integer parameter to choose type of capillary pressure function (see Appendix H).

CP(I) I = 1, ..., 7 parameters for capillary pressure function (Appendix H).

Repeat records 1, 1.1, 1.2, and 1.3 for up to 27 reservoir domains.

Record ROCKS.2 A blank record closes the ROCKS data block.

CHEMP provides data for calculating the thermophysical properties of the NAPL/chemical. The units of many of these constants are not standard metric units, and care must be taken to ensure that the appropriate units are used. Most of the data used in this block can be taken from Appendix A of Reid et al. (1987), where the same units are used as here.

CHEMP has the same data formats as for T2VOC, except that for TMVOC there are two new data records, CHEMP.1 and CHEMP.2. These provide, respectively, the number of organic components used in TMVOC (≤ 18), and the name of the component for which data are being provided.

Record CHEMP.1

Format(I5)
NHC

NHC number of organic chemicals for which data are to be entered. When using NK = 2 (water and air only, no VOCs) NHC must be set to zero. Subsequent CHEMP records can be omitted in this case.

Record CHEMP.2

Format(A20)
HCNAMES

HCNAMES name of the organic chemical (identification only; no effect on calculations).

Record CHEMP.3

Format (5E10.4)
TCRITM, PCRITM, ZCRITM, OMEGAM, DIPOLMM

TCRITM chemical critical temperature, K.

PCRITM chemical critical pressure, bar (1 bar = 10^5 Pa).

ZCRITM chemical critical compressibility.

OMEGAM Pitzer's acentric factor for the chemical.

DIPOLMM chemical dipole moment, debyes.

Record CHEMP.4

Format (5E10.4)
TBOILM, VPAM, VPBM, VPCM, VPDM

TBOILM chemical normal boiling point, K.

VPAM chemical vapor pressure constant from Reid et al. (1987).
If VPAM ≠ 0 use Wagner correlation (Reid et al., 1987), for VPAM = 0 use Antoine correlation.

VPBM chemical vapor pressure constant from Reid et al. (1987).

VPCM chemical vapor pressure constant from Reid et al. (1987).

VPDM chemical vapor pressure constant from Reid et al. (1987).

Record CHEMP.5

Format (5El0.4)
AMWTM, CPAM, CPBM, CPCM, CPDDM

AMWTM chemical molecular weight, g/mole.

CPAM chemical ideal gas heat capacity constant from Reid et al. (1987).

CPBM chemical ideal gas heat capacity constant from Reid et al. (1987)

CPCM chemical ideal gas heat capacity constant from Reid et al. (1987).

CPDDM chemical ideal gas heat capacity constant from Reid et al. (1987).

Record CHEMP.6

Format (5El0.4)
RHOREFM, TDENREF, DIFV0M, TDIFREF, TEXPOM

RHOREFM reference NAPL (liquid) density, kg/m^3.

TDENREF reference temperature for NAPL density, K.

DIFV0M reference binary diffusivity of VOC in air, m^2/s.

TDIFREF reference temperature for gas diffusivity, K.

TEXPOM exponent for calculation of chemical diffusivity.

Record CHEMP.7 introduces data for NAPL viscosity.

Format (5El0.4)
VLOAM, VLOBM, VLOCM, VLODM, VOLCRITM

Two options are available for calculating the NAPL liquid viscosity. The liquid viscosity constants VLOAM - VLODM for the desired NAPL may be assigned data given in Table 9-8 of Reid et al. (1987), and the viscosity will be calculated using a polynomial fit to actual viscosity data (Eq. 4.3.11). Alternatively, VLOAM and VLOBM may be set equal to 0, and VLOCM and VLODM are assigned equal to a reference viscosity and a reference temperature, respectively. In this case, the viscosity is calculated from a more general (and less accurate) empirical correlation (Van Velzen et al., 1972).

VLOAM liquid NAPL viscosity constant from Reid et al. (1987).

VLOBM liquid NAPI viscosity constant from Reid et al. (1987).

VLOCM liquid NAPL viscosity constant from Reid et al. (1987).
If VLOAM and VLOBM = 0, VLOCM is reference NAPL viscosity in units of cP (1 cP = 10^{-3} Pa-s).

VLODM liquid NAPL viscosity constant from Reid et al. (1987).
If VLOAM and VLOBM = 0, VLODM is reference temperature for NAPL viscosity in units of Kelvin.

VOLCRITM chemical critical volume, $cm^3/mole$.

Record CHEMP.8 introduces data for chemical solubility.

Fomat (4E10.4)
SOLAM, SOLBM, SOLCM, SOLDM

The chemical solubility is calculated from the polynomial SOLUBILITY = SOLAM + SOLBM*T + SOLCM*T**2 + SOLDM*T**3. If data for the solubility as a function of temperature are available, then SOLAM, SOLBM, SOLCM, and SOLDM should be calculated from a polynomial fit

of the data. If such data are not available (the usual case), the solubility will be assumed to be constant, and SOLAM should be set equal to the known solubility, with SOLBM, SOLCM, and SOLDM set equal to 0.

SOLAM constant for chemical solubility in water, mole fraction.

SOLBM constant for chemical solubility in water, mole fraction/K.

SOLCM constant for chemical solubility in water, mole fraction/K^2.

SOLDM constant for chemical solubility in water, mole fraction/K^3.

Record CHEMP.9

Fomat (3El0.4)
OCKM, FOXM, ALAMM

OCKM chemical organic carbon partition coefficient K_{oc} (see Eq. 4.4.2), m^3/kg.

FOXM default value for fraction of organic carbon in soil, used for all domains for which no specific value is provided in record ROCKS.1.1.

ALAMM decay constant for biodegradation of VOC, s^{-1} (see section 4.5). Biodegradation is assumed to take place only in the aqueous phase, and to follow a first order decay law, $M_{VOC}(t) = M_{VOC,0} * \exp(-\lambda t)$. The decay constant λ = ALAMM is expressed in terms of the half life $T_{1/2}$ of the VOC as follows: $\lambda = (\ln 2) / T_{1/2}$. Default is ALAMM = 0.

Repeat records CHEMP.2 through CHEMP.9 for a total of NHC (up to eighteen) different organic chemicals.

NCGAS is an optional data block for specifying the number and nature of non-condensible gases to be modeled by TMVOC. If NCGAS is absent, there will be a single non-condensible gas, air.

Record NCGAS.1

Format (I5)
NCG

NCG number of non-condensible gases in the simulation.

Record NCGAS.2

Format (A10)
NCGINP

NCGINP name of non-condensible gas, to be chosen among the 8 NCGs included in the internal data bank. They are: AIR, O2, N2, CO2, CH4, ETHANE, ETHYLENE, ACETYLENE. NCG names are case sensitive and must be entered exactly as stated here, starting in column 1.

Provide record NCGAS.2 for NCG non-condensible gases as specified in record NCGAS.1.

MULTI is a mandatory data block for TMVOC which permits the user to select the number and nature of balance equations that will be solved. MULTI must precede data blocks PARAM, INDOM, and INCON (if present). The keyword MULTI is followed by a single data record.

Record MULTI.1

Format (5I5)
NK, NEQ, NPH, NB, NKIN

NK (≥ 2) number of mass components. By convention, mass component # 1 is water, # 2 through NCG+1 are the NCGs, and components # NCG+2 through NK = NHC+NCG+1 are the VOCs (see Table 3). By specifying NK = 2 a run with only water and air and no VOCs can be performed. In this case parameter NHC in data block CHEMP must be set to zero.

NEQ number of balance equations per grid block.
Usually we have NEQ = NK + 1, for solving NK mass and one energy balance equation. TMVOC allows the option NEQ = NK, in which case only NK mass balances and no energy equation will be solved. However, even when specifying NEQ = NK temperatures in different grid blocks may be different. Initial temperatures will remain unchanged in the course of a simulation, and all thermophysical properties will be evaluated at the temperatures specified for the individual grid blocks.

NPH number of phases that can be present. Only available option is NPH = 3.

NB number of secondary parameters in the PAR-array (see Fig. 6.3.1) other than component mass fractions. Available options include NB = 6 (no diffusion) and NB = 8 (include diffusion).

NKIN (≥ 2) number of mass components in INCON data (default is NKIN = NK). This parameter can be used to initialize a simulation with NK mass components from initial conditions for NKIN < NK components. For example, the user may first run a simulation with NK = 2 (water and air only, no VOCs), to obtain "natural" state conditions prior to a contamination event. The SAVE file generated by that run can be used as INCON (data or file) in a subsequent run with NKIN = 2, NK > NKIN, in which a VOC release will be modeled. By convention, the mass components NKIN+1, NKIN+2, ... will be initialized with concentrations equal to 0. Only VOCs (not NCGs) can be added when running with NK > NKIN.

A TMVOC simulation may be optionally initialized from T2VOC-style primary variables by setting NKIN to the negative of the number of mass components in the T2VOC data; i.e., NKIN = -2 or -3. For consistency, if this option is used TMVOC should run with only one NCG, and this should be air. If the same temperature-independent Henry's coefficient K_H is to be used as in T2VOC, IE(3) = 1 must be specified in data block SELEC. Further explanation of initialization and primary variable useage is given in the section on data block PARAM below (records PARAM.4 and PARAM.5).

START (optional)

A record with START typed in columns 1-5 allows a more flexible initialization. More specifically, when START is present, INCON data can be in arbitrary order, and need not be present for all grid blocks (in which case defaults will be used). Without START, there must be a one-to-one correspondence between the data in blocks ELEME and INCON.

PARAM introduces computation parameters, time stepping information, and default initial conditions.

Record PARAM.1

Format (2I2, 3I4, 24I1, 10X, 2E10.4).
NOITE, KDATA, MCYC, MSEC, MCYPR, (MOP(I), I = 1, 24), TEXP, BE

NOITE specifies the maximum number of Newtonian iterations per time step (default is 8). Time step will be reduced if no convergence is achieved.

KDATA specifies amount of printout (default is 1).

0 or 1: print a selection of the most important variables.

2: in addition, print mass and heat fluxes and flow velocities.

3: in addition, print primary variables and their changes.

If the above values for KDATA are increased by 10, printout will occur after each Newton-Raphson iteration (not just after convergence).

MCYC maximum number of time steps to be calculated.

MSEC maximum duration, in CPU seconds, of the simulation (default is infinite).

MCYPR printout will occur for every multiple of MCYPR steps (default is 1).

MOP(I), I = 1,24 allows choice of various options, which are documented in printed output from a TMVOC run.

MOP(1) if unequal 0, a short printout for non-convergent iterations will be generated.

MOP(2) through MOP(6) generate additional printout in various subroutines, if set unequal 0. This feature should not be needed in normal applications, but it will be convenient when a user suspects a bug and wishes to examine the inner workings of the code. The amount of printout increases with MOP(I) (consult source code listings for details).

MOP(2) CYCIT (main subroutine).

MOP(3) MULTI (flow- and accumulation-terms).

MOP(4) QU (sinks/sources).

MOP(5) EOS (equation of state).

MOP(6) LINEQ (linear equations).

MOP(7) if unequal 0, a printout of input data will be provided.

MOP(8) not used by TMVOC.

Calculational choices are as follows:

MOP(9) determines the composition of produced fluid with the MASS option (see GENER, below). The relative amounts of phases are determined as follows:

0: according to relative mobilities in the source element.

1: produced source fluid has the same phase composition as the producing element.

MOP(10) chooses the interpolation formula for heat conductivity as a function of liquid saturation (S_l)

0: $C(S_l) = CDRY + SQRT(S_l * [CWET - CDRY])$

1: $C(S_l) = CDRY + S_l * (CWET - CDRY)$

MOP(11) determines evaluation of mobility and permeability at interfaces.

0: mobilities are upstream weighted with WUP (see PARAM.3), permeability is upstream weighted.

1: mobilities are averaged between adjacent elements, permeability is upstream weighted.

2: mobilities are upstream weighted, permeability is harmonic weighted.

3: mobilities are averaged between adjacent elements, permeability is harmonic weighted.

4: mobility and permeability are both harmonic weighted.

MOP(12) determines interpolation procedure for time dependent sink/source data (flow rates and enthalpies).

0: triple linear interpolation; tabular data are used to obtain interpolated rates and enthalpies for the beginning and end of the time step; the average of these values is then used.

1: step function option; rates and enthalpies are taken as averages of the table values corresponding to the beginning and end of the time step.

2: rigorous step rate capability for time dependent generation data.

A set of times t_i and generation rates q_i provided in data block GENER is interpreted to mean that sink/source rates are piecewise constant and change in discontinuous fashion at table points. Specifically, generation is assumed to occur at constant rate q_i during the time interval $[t_i, t_{i+1})$, and changes to q_{i+1} at t_{i+1}. Actual rate used during a time step that ends at time t, with $t_i \le t \le t_{i+1}$, is automatically adjusted in such a way that total cumulative exchanged mass at time t

$$Q(t) = \int_0^t q\,dt' = \sum_{j=1}^{i-1} q_j (t_{j+1} - t_j) + q_i (t - t_i) \qquad \text{(E.1)}$$

is rigorously conserved. If also tabular data for enthalpies are given, an analogous adjustment is made for fluid enthalpy, to preserve $\int qh\,dt$.

MOP(13) (used by dispersion module T2DM).

MOP(14) determines handling of pivot failures in matrix decomposition (MA28 only).

0: perform new matrix decomposition when encountering a pivot failure.

>0: ignore pivot failures.

MOP(15) determines conductive heat exchange with impermeable confining layers (see section 8.4).

0: heat exchange is off.

1: heat exchange is on (for grid blocks that have a non-zero heat transfer area; see data block ELEME).

MOP(16) provides automatic time step control. Time step size will be doubled if convergence occurs within ITER ≤ MOP(16) Newton-Raphson iterations. It is recommended to set MOP(16) in the range of 2 - 4.

MOP(17) chooses scaling-option for preconditioning the Jacobian matrix (MA28 only).

0: no scaling.

7: do perform scaling.

MOP(18) selects handling of interface density.

0: perform upstream weighting for interface density.

>0: average interface density between the two grid blocks. However, when one of the two phase saturations is zero, upstream weighting will be performed.

MOP(19) (not used by TMVOC).

MOP(20) (switch for vapor pressure lowering in EOS4 of TOUGH2).

MOP(21) selects the linear equation solver (see section 8.6).

0: defaults to MOP(21) = 3, DSLUCS, Lanczos-type preconditioned bi-conjugate gradient solver.

1: MA28, sparse direct solver.

2: DSLUBC, bi-conjugate gradient solver.

3: DSLUCS (default).

4: DSLUGM, generalized minimum residual preconditioned conjugate gradient solver.

5: DLUSTB, stabilized bi-conjugate gradient solver.

6: LUBAND, banded direct solver.

All conjugate gradient solvers use incomplete LU-factorization as a default preconditioner. Other preconditioners may be chosen by means of a data block SOLVR (see section 8.6).

MOP(22) (used by dispersion module T2DM).

MOP(23) (used by dispersion module T2DM).

MOP(24) determines handling of multiphase diffusive fluxes at interfaces.

0: harmonic weighting of fully coupled effective multiphase diffusivity.

1: separate harmonic weighting of gas and liquid phase diffusivities.

TEXP parameter for temperature dependence of gas phase diffusion coefficient (see Eq. D.8).

BE (optional) parameter for effective strength of enhanced vapor diffusion; if set to a non-zero value, will replace the parameter group $\phi\tau_0\tau_\beta$ for vapor diffusion (see Eq. D.3 and section D.4).

Record PARAM.2

Format (4E10.4, A5, 5X,3E10.4)
TSTART, TIMAX, DELTEN, DELTMX, ELST, GF, REDLT, SCALE

TSTART starting time of simulation in seconds (default is 0).

TIMAX time in seconds at which simulation should stop (default is infinite).

DELTEN — length of time steps in seconds. If DELTEN is a negative integer, DELTEN = -NDLT, the program will proceed to read NDLT records with time step information. Note that - NDLT must be provided as a floating point number, with decimal point.

DELTMX — upper limit for time step size in seconds (default is infinite).

ELST — set equal to the name of one element to obtain a short printout after each time step.

GF — magnitude (m/sec^2) of the gravitational acceleration vector. Blank or zero gives "no gravity" calculation.

REDLT — factor by which time step is reduced in case of convergence failure or other problems (default is 4).

SCALE — scale factor to change the size of the mesh (default = 1.0).

Record PARAM.2.1, 2.2, etc.

Format (8E10.4)
(DLT(I), I = 1, 100)

DLT(I) — Length (in seconds) of time step I.

This set of records is optional for DELTEN = - NDLT, a negative integer. Up to 13 records can be read, each containing 8 time step data. If the number of simulated time steps exceeds the number of DLT(I), the simulation will continue with time steps equal to the last non-zero DLT(I) encountered. When automatic time step control is chosen (MOP(16) > 0), time steps following the last DLT(I) input by the user will increase according to the convergence rate of the Newton-Raphson iteration. Automatic time step reduction will occur if the maximum number of Newton-Raphson iterations is exceeded (parameter NOITE, record PARAM.1).

Record PARAM.3

Format (6E10.4,10X,E10.4)
RE1, RE2, U, WUP, WNR, DFAC, AMRES

RE1 — convergence criterion for relative error, see Appendix B (default= 10^{-5}).

RE2 — convergence criterion for absolute error, see appendix B (default= 1).

U — pivoting parameter for linear equation solution with the MA28 direct solver. U must be in the range $0 \leq U < 1$, and the default is U = 0.1. Increased value for U will make criterion for pivot selection more stringent, resulting in better numerical stability at the expense of increased computing time for matrix decomposition.

WUP — upstream weighting factor for mobilities and enthalpies at interfaces

(default = 1.0 is recommended). $0 \leq WUP \leq 1$.

WNR weighting factor for increments in Newton/Raphson - iteration (default = 1.0 is recommended). $0 < WNR \leq 1$.

DFAC increment factor for numerically computing derivatives (default value is $DFAC = 10^{-k/2}$, where k, evaluated internally, is the number of significant digits of the floating point processor used; for 64-bit arithmetic, $DFAC \approx 10^{-8}$).

AMRES maximum permissible residual during the Newtonian iteration (Eq. B.8). If a residual larger than AMRES is encountered, time step will automatically be reduced. When AMRES is left blank or is set to zero, no limitation on residuals will be enforced.

Record PARAM.4 (only for TMVOC-style initialization; absent when T2VOC-style initial conditions are used).

Format(I5)
INDICAT0

INDICAT0 integer variable to specify default phase compositions for all grid blocks that are not given alternative assignments by means of data blocks INDOM or INCON. Parameters corresponding to the seven possible phase combinations in a gas-water-oil system are shown in Table E.1. Option START is necessary to use default initial conditions.

Record PARAM.5 introduces a set of primary variables which are used as default initial conditions for all grid blocks that are not assigned by means of data blocks INDOM or INCON. The primary thermodynamic variables used in TMVOC depend on the phase conditions and are summarized in Table E.1, below.

Format (4E20.14)
DEP(I), I = 1, NKIN+1

Table E.1. Phase identifiers (INDICAT0) and primary thermodynamic variables used by TMVOC.

Phase Conditions	Phase Index	Primary Variables ⇐ ⇐ ⇐ ⇐ VOCs ⇐ | ⇒ NCGs ⇒ ⇒ ⇒ ⇒							
			VOC #1	···	VOC #NHC	NCG #1	···	NCG #NCG	
		1	2	···	NHC + 1	NHC + 2	···	NK	NK+1
gas only	1	P	x_g^{2+NCG}	...	x_g^{NK}	x_g^2	...	x_g^{1+NCG}	T
water only	2	P	x_w^{2+NCG}	...	x_w^{NK}	x_w^2	...	x_w^{1+NCG}	T
NAPL only	3	P	x_n^{2+NCG}	...	x_n^{NK}	x_n^2	...	x_n^{1+NCG}	T
gas and water	4	P	x_g^{2+NCG}	...	x_g^{NK}	x_g^2	...	S_w	T
gas and NAPL	5	P	x_g^{2+NCG}	...	x_g^{NK}	x_g^2	...	S_n	T
water and NAPL	6	P	x_n^{2+NCG}	...	x_n^{NK}	x_n^2	...	S_w	T
three phase	7	P	S_g	...	x_g^{NK}	x_g^2	...	S_w	T

P is the pressure of a reference phase in units of Pa. Actual pressure used in each of the phases is P + $P_{c\beta}$, where $P_{c\beta}$ is capillary pressure in phase β = g, w, n at prevailing saturation conditions. x_β^ν are mole fractions of the ν = 1, ..., NHC+NCG hydrocarbon and NCG components in the different phases; S_β is saturation of phase β; and T is temperature in °C. When more than four primary variables are used, more than one line (record) of input data must be provided.

For NKIN < 0 (NKIN = -2 or -3) T2VOC-style primary variables as shown in Table E.2 are used for initialization (see discussion of data block MULTI, above), and record PARAM.4 is omitted..

Table E.2. Choice of primary variables in T2VOC.

Primary Variables / Phases	X1	X2	X3	X4
aqueous	P	Xaw+50	Xmolow	T
aq., NAPL	P	Sw	Xaw+50	T
aq., gas	P	Sw	Xmolog	T
aq., gas, NAPL	P	Sw	Sg+10	T

Specifically, for NKIN = -3 the run is initialized from NK = 3 T2VOC-style variables, while for NKIN = -2 initialization is made from NK = 2 T2VOC-style variables. For NK = 2 in T2VOC the third primary variable is omitted. When using T2VOC-style primary variables, these will be converted internally to TMVOC-type variables during the initialization phase of a simulation. TMVOC always uses the primary variables as given in Table E.1.

The T2VOC primary variables are P - pressure, Xaw - mass fraction of air in aqueous phase, Xmolow - mole fraction of VOC in aqueous phase, T - temperature, Sw - water saturation, Xmolog - mole fraction of VOC in gas phase, and Sg - gas saturation. The increments (adding 10, 50) and place changes for some of the primary variables have been chosen so as to enable the fluid property module to recognize fluid phase compositions from the numerical values of the primary variables present.

INDOM introduces domain-specific initial conditions. These will supersede default initial conditions specified in PARAM.4, 5 and can be overwritten by element-specific initial conditions in data block INCON. Option START is needed to use INDOM conditions.

Data formats for record INDOM.2 are identical to those for record PARAM.5.

Record INDOM. 1

Format(A5, I5)
MAT, INDECEIN

MAT name of a reservoir domain, as specified in data block ROCKS.

INDECEIN integer variable to specify default phase compositions for all grid blocks in the domain named in record INDOM.1. These may be superseded for individual grid blocks by means of assignments in data block INCON. See explanation given for parameter INDICAT0 (record PARAM.4, above). For NKIN = -2 or -3 (data block MULTI), thermodynamic conditions are input as for T2VOC, and are converted internally to TMVOC format. In that case parameter INDECEIN can be omitted and will be ignored.

Record INDOM.2

Format(4E20.13)
Xl, X2, X3, ...

A set of NKIN+1 primary variables assigned to all grid blocks in the domain specified in record INDOM.l. See Table E.1 for information on the primary variables.

Repeat records INDOM. l and INDOM.2 for as many domains as desired. The ordering is arbitrary and need not be the same as in block ROCKS.

Record INDOM.3

A blank record closes the INDOM data block.

INCON introduces element-specific initial conditions.

Record INCON.1

Format (A3, I2, 2I5, E15.9, I2)
EL, NE, NSEQ, NADD, PORX, INDICEE

EL, NE code name of element.

NSEQ number of additional elements with the same initial conditions.

NADD increment between the code numbers of two successive elements with identical initial conditions.

PORX porosity; if zero or blank, porosity will be taken as specified in block ROCKS if option START is used.

INDICEE integer variable to assign phase compositions for specific grid blocks. For parameter choices see the explanation given for parameter INDICAT0 (record PARAM.4, above). When T2VOC-style initial conditions are used, parameter INDICEE is ignored.

Record INCON.2 specifies primary variables.

Format (4E20.14)
Xl, X2, X3, ...

A set of NKIN+1 primary variables for the element specified in record INCON.l. Data formats are identical to record PARAM.5. INCON specifications will supersede default conditions specified in PARAM.4,5, and will supersede domain-specific conditions that may have been specified in data block INDOM.

Record INCON.3 A blank record closes the INCON data block. Alternatively, initial condition information may terminate on a record with '+++' typed in the first three columns, followed by time stepping information. This feature is used for a continuation run from a previous TMVOC simulation.

SOLVR (optional) introduces a data block with parameters for linear equation solvers.

Record SOLVR.1

Format(I1,2X,A2,3X,A2,2E10.4)

MATSLV, ZPROCS, OPROCS, RITMAX, CLOSUR

The SOLVR parameter choices are explained in section 8.6.

FOFT (optional) introduces a list of elements (grid blocks) for which time-dependent data are to be written out for plotting to a file called FOFT during the simulation.

Record FOFT.1

Format(A5)
EOFT(I)

EOFT is an element name. Repeat for up to 100 elements, one per record.

Record FOFT.2 A blank record closes the FOFT data block.

COFT (optional) introduces a list of connections for which time-dependent data are to be written out for plotting to a file called COFT during the simulation.

Record COFT.1

Format(A10)
ECOFT(I)

ECOFT is a connection name, i.e., an ordered pair of two element names. Repeat for up to 100 connections, one per record.

Record COFT.2 A blank record closes the COFT data block.

GOFT (optional) introduces a list of sinks/sources for which time-dependent data are to be written out for plotting to a file called GOFT during the simulation.

Record GOFT.1

Format(A5)
EGOFT(I)

EGOFT is the name of an element in which a sink/source is defined. Repeat for up to 100 sinks/sources, one per record. When no sinks or sources are specified here, by default tabulation will be made for all.

Record GOFT.2 A blank record closes the GOFT data block.

NOVERSION (optional)

One record with NOVER typed in columns 1-5 will suppress printing of a summary of versions and dates of the program units in a TMVOC run.

SELECTION (optional) introduces a number of integer and floating point parameters that are used for different purposes in different TOUGH2 modules.

Record SELEC.1

Format(16I5)
IE(I), I=1,16

IE(1) number of records with floating point numbers that will be read (default for IE(1) = 0 is one additional record; maximum value is 64).

IE(2) allows to choose among different EOS options for real gas mixture.

0: Soave-Redlich-Kwong (Soave, 1972); default.

-1: ideal gas mixture.

1: Soave-Redlich-Kwong (Soave, 1972).

2: modified Soave-Redlich-Kwong (Graboski et al., 1978).

3: Peng-Robinson (Peng and Robinson, 1976).

IE(3) allows to choose different correlations for air solubility in water

0: $K_H = K_H(T)$, as in EWASG (Battistelli et al., 1997).

1: $K_H = 10^{10}$ Pa, independent of temperature, as in EOS3 and T2VOC.

2: K_H for air is obtained by harmonic weighting of the Henry's coefficients for oxygen and nitrogen.

Record SELEC.2, SELEC.3, ..., SELEC.IE(1)*8

Format(8E10.4)
FE(I), I=1,IE(1)*8

provide as many records with floating point numbers as specified in IE(1), up to a maximum of 64 records; default for IE(1) = 0 is one additional record. Presently no use is made of these parameters in TMVOC.

DIFFUSION (optional; needed only for NB ≥ 8) introduces diffusion coefficients.

Record DIFFU.1

Format(8E10.4)
FDDIAG(I,1), I=1,NPH
diffusion coefficients for mass component # 1 in all phases (I=1: gas; I=2: aqueous; I=3: NAPL).

Record DIFFU.2

Format(8E10.4)
FDDIAG(I,2), I=1,NPH
diffusion coefficients for mass component # 2 in all phases.

provide a total of NK records with diffusion coefficients for all NK mass components. See Appendix D for additional parameter specifications for diffusion.

RPCAP introduces information on relative permeability and capillary pressure functions, which will be applied for all flow domains for which no data were specified in records ROCKS.1.2 and ROCKS.1.3. A catalog of relative permeability and capillary pressure functions is presented in Appendix G and Appendix H, respectively.

Record RPCAP.1

Format (I5,5X,7E10.4)
IRP, (RP(I),I = 1, 7)

IRP integer parameter to choose type of relative permeability function (see Appendix G).

RP(I), I = 1, ..., 7 parameters for relative permeability function (Appendix G).

Record RPCAP.2

Format (I5,5X,7E10.4)
ICP, (CP(I), I = 1, 7)

ICP integer parameter to choose type of capillary pressure function (see Appendix H).

CP(I) I = 1, ..., 7 parameters for capillary pressure function (Appendix H).

TIMES permits the user to obtain printout at specified times (optional). This printout will occur in addition to printout specified in record PARAM.1.

Record TIMES.1

Format (2I5,2E10.4)
ITI, ITE, DELAF, TINTER

ITI number of times provided on records TIMES.2, TIMES.3, etc., (see below; restriction: ITI ≤ 100).

ITE total number of times desired (ITI ≤ ITE ≤ 100; default is ITE = ITI).

DELAF maximum time step size after any of the prescribed times have been reached (default is infinite).

TINTER time increment for times with index ITI, ITI+1, ..., ITE.

Record TIMES.2, TIMES.3, etc.

Format (8E10.4)
(TIS(I), I = l, ITI)

TIS(I) list of times (in ascending order) at which printout is desired.

ELEME introduces element (grid block) information.

Record ELEME.1

Format (A3, I2, 2I5, A3, A2, 6E10.4)
EL, NE, NSEQ, NADD, MA1, MA2, VOLX, AHTX, PMX, X, Y, Z

EL, NE — five-character code name of an element. The first three characters are arbitrary, the last two characters must be numbers.

NSEQ — number of additional elements having the same volume and belonging to the same reservoir domain.

NADD — increment between the code numbers of two successive elements. (Note: the maximum permissible code number NE + NSEQ *NADD is ≤ 99.)

MA1, MA2 — a five-character material identifier corresponding to one of the reservoir domains as specified in block ROCKS. If the first three characters are blanks and the last two characters are numbers then they indicate the sequence number of the domain as entered in ROCKS. If both MA1 and MA2 are left blank the element is by default assigned to the first domain in block ROCKS.

VOLX — element volume (m^3).

AHTX — interface area (m^2) for heat exchange with semi-infinite confining beds. Internal MESH generation via MESHMaker will automatically assign AHTX.

PMX — permeability modifier (optional, active only when a domain 'SEED ' has been specified in the ROCKS block; see section 8.5). Will be used as multiplicative factor for the permeability parameters from block ROCKS. Simultaneously, strength of capillary pressure will be scaled as 1/SQRT(PMX). PMX = 0 will result in an impermeable block.

Random permeability modifiers can be generated internally, see detailed comments in the TMVOC output file. The PMX may be used to specify spatially correlated heterogeneous fields, but users need their own preprocessing programs for this, as TMVOC provides no internal capabilities for generating such fields.

X, Y, Z — Cartesian coordinates of grid block centers. These may be included in the ELEME data to make subsequent plotting of results more convenient. The coordinate data are not used in TMVOC.

Repeat record ELEME.1 for the number of elements desired.

Record ELEME.2 A blank record closes the ELEME data block.

CONNE introduces information for the connections (interfaces) between elements.

Record CONNE.1

Format (A3, I2, A3, I2, 4I5, 5E10.4)
EL1, NE1, EL2, NE2, NSEQ, NAD1, NAD2, ISOT, D1, D2, AREAX, BETAX, SIGX

EL1, NE1 code name of the first element.

EL2, NE2 code name of the second element.

NSEQ number of additional connections in the sequence.

NAD1 increment of the code number of the first element between two successive connections.

NAD2 increment of the code number of the second element between two successive connections.

ISOT set equal to 1, 2, or 3; specifies absolute permeability to be PER(ISOT) for the materials in elements (EL1, NE1) and (EL2, NE2), where PER is read in block ROCKS. This allows assignment of different permeabilities, e.g., in the horizontal and vertical direction.

D1 } distance (m) from first and second element, respectively, to their common
D2 } interface.

AREAX interface area (m^2).

BETAX cosine of the angle between the gravitational acceleration vector and the line between the two elements. GF * BETAX > 0 (<0) corresponds to first element being above (below) the second element.

SIGX "radiant emittance" factor for radiative heat transfer, which for a perfectly "black" body is equal to 1. The rate of radiative heat transfer between the two grid blocks is

$$G_{rad} = SIGX * \sigma_0 * AREAX * (T_2^4 - T_1^4) \qquad (E.2)$$

where σ_0 = 5.6687e-8 J/m^2 K^4 s is the Stefan-Boltzmann constant, and T_1 and T_2 are the absolute temperatures of the two grid blocks. SIGX may be entered as a negative number, in which case the absolute value will be used, and heat conduction at the connection will be suppressed. SIGX = 0 will result in no radiative heat transfer.

Repeat record CONNE.1 for the number of connections desired.

Record CONNE.2 A blank record closes the CONNE data block. Alternatively, connection information may terminate on a record with '+++' typed in the first three columns, followed by element cross-referencing information. This is the termination used when generating a MESH file with TMVOC.

GENER introduces sinks and/or sources.

Record GENER.1

Format (A3, I2, A3, I2, 4I5, 5X,A4, A1,3E10.4)
EL, NE, SL, NS, NSEQ, NADD, NADS, LTAB, TYPE, ITAB, GX, EX, HX

EL, NE code name of the element containing the sink/source.

SL, NS code name of the sink/source. The first three characters are arbitrary, the last two characters must be numbers.

NSEQ number of additional sinks/sources with the same injection/production rate (not applicable for TYPE = DELV).

NADD increment between the code numbers of two successive elements with identical sink/source.

NADS increment between the code numbers of two successive sinks/sources.

LTAB number of points in table of generation rate versus time. Set 0 or 1 for constant generation rate. For wells on deliverability, LTAB denotes the number of open layers, to be specified only for the bottommost layer.

TYPE specifies different options for fluid or heat production and injection.

HEAT introduces a heat sink/source.

COM1 WATE	- component 1 (water).	injection only	
COM2	- component 2 (NCG # 1)		
COM3	- component 3 (NCG # 2)		
• • •			
COMn	- component n (VOC # n-ncg-1)		

If the component index n is larger than 9, use TYPE = CO10, CO11 etc.

MASS - mass production rate specified.

DELV - well on deliverability, i.e., production occurs against specified bottomhole pressure. If well is completed in more than one layer, bottommost layer must be specified first, with number of layers given in LTAB. Subsequent layers must be given sequentially for a total number of LTAB layers.

ITAB — unless left blank, table of specific enthalpies will be read (LTAB > 1 only). When fluid injection is specified as time-dependent tabular data (LTAB > 1), ITAB must be set to a non-blank character, and enthalpy data must be provided (F3, below).

GX — constant generation rate; positive for injection, negative for production; GX is mass rate (kg/sec) for generation types COMl, COM2, COM3, etc., and MASS; it is energy rate (J/s) for a HEAT sink/source. For wells on deliverability, GX is productivity index PI (m^3), Eq. (29).

EX — fixed specific enthalpy (J/kg) of the fluid for mass injection (GX>0). For wells on deliverability against fixed bottomhole pressure, EX is bottomhole pressure P_{wb} (Pa), at the center of the topmost producing layer in which the well is open.

HG — thickness of layer (m; wells on deliverability with specified bottomhole pressure only).

Record GENER.l.l (optional, LTAB > l only)

Format (4E14.7)
Fl(L), L=l, LTAB

F1 — generation times

Record GENER.1.2 (optional, LTAB > 1 only)

Format (4E14.7)
F2(L), L=1, LTAB

F2 — generation rates.

Record GENER.1.3 (LTAB > 1 and ITAB non-blank only; optional for fluid production (F2 < 0), mandatory for fluid injection (F2 > 0))

Format (4E14.7)
F3(L), L=1, LTAB

F3 — specific enthalpy of produced or injected fluid.

Repeat records GENER.1, 1.1, 1.2, and 1.3 for the number of sinks/sources desired.

Record GENER.2 — A blank record closes the GENER data block. Alternatively, generation information may terminate on a record with '+++' typed in the first three columns, followed by element cross-referencing information.

ENDCY — closes the TMVOC input file and initiates the simulation.

Note on closure of blocks CONNE, GENER, and INCON

The ordinary way to indicate the end of any of the above data blocks is by means of a blank record. There is an alternative available if the user makes up an input file from files MESH, GENER, or SAVE, which have been generated by a previous TMVOC run. These files are written exactly according to the specifications of data blocks ELEME and CONNE (file MESH), GENER (file GENER), and INCON (file SAVE), except that the CONNE, GENER, and INCON data terminate on a record with "+++" in columns 1-3, followed by some cross-referencing and restart information. TMVOC will accept this type of input, and in this case there is no blank record at the end of the indicated data blocks.

Appendix F. Input Formats for MESHMAKER

The MESHMaker module performs internal mesh generation and processing. The input for MESHMaker has a modular structure and a variable number of records; it begins with keyword MESHM and ends with a blank record (see Fig. F.1).

At the present time there are three sub-modules available in MESHMaker**:** keywords RZ2D or RZ2DL invoke generation of a one or two-dimensional radially symmetric R-Z mesh; XYZ initiates generation of a one, two, or three dimensional Cartesian X-Y-Z mesh; and MINC calls a modified version of the GMINC program (Pruess, 1983b) to sub-partition a primary porous medium mesh into a secondary mesh for fractured media, using the method of "multiple interacting continua" (Pruess and Narasimhan, 1982, 1985). The meshes generated under keyword RZ2D or XYZ are internally written to file MESH. The MINC processing operates on the data in file MESH, so that invoking the RZ2D or XYZ options, or assignment of ELEME and CONNE blocks in the INPUT file must precede the MESHMaker/MINC data. We shall now separately describe the preparation of input data for the three MESHMaker sub-modules.

Generation of radially symmetric grids

Keyword RZ2D (or RZ2DL) invokes generation of a radially symmetric mesh. Values for the radii to which the grid blocks extend can be provided by the user or can be generated internally (see below). Nodal points will be placed half-way between neighboring radial interfaces. When RZ2D is specified, the mesh will be generated by columns; i.e., in the ELEME block we will first have the grid blocks at smallest radius for all layers, then the next largest radius for all layers, and so on. With keyword RZ2DL the mesh will be generated by layers; i.e., in the ELEME block we will first have all grid blocks for the first (top) layer from smallest to largest radius, then all grid blocks for the second layer, and so on. Apart from the different ordering of elements, the two meshes for RZ2D and RZ2DL are identical. The reason for providing the two alternatives is as a convenience to users in implementing boundary conditions by way of inactive elements (see Section 8.2). Assignment of inactive elements would be made by using a text editor on the RZ2D-generated MESH file, and moving groups of elements towards the end of the ELEME block, past a dummy element with zero volume. RZ2D makes it easy to declare a vertical column inactive, facilitating assignment of boundary conditions in the vertical, such as a gravitationally equilibrated pressure gradient. RZ2DL on the other hand facilitates implementation of areal (top and bottom layer) boundary conditions.

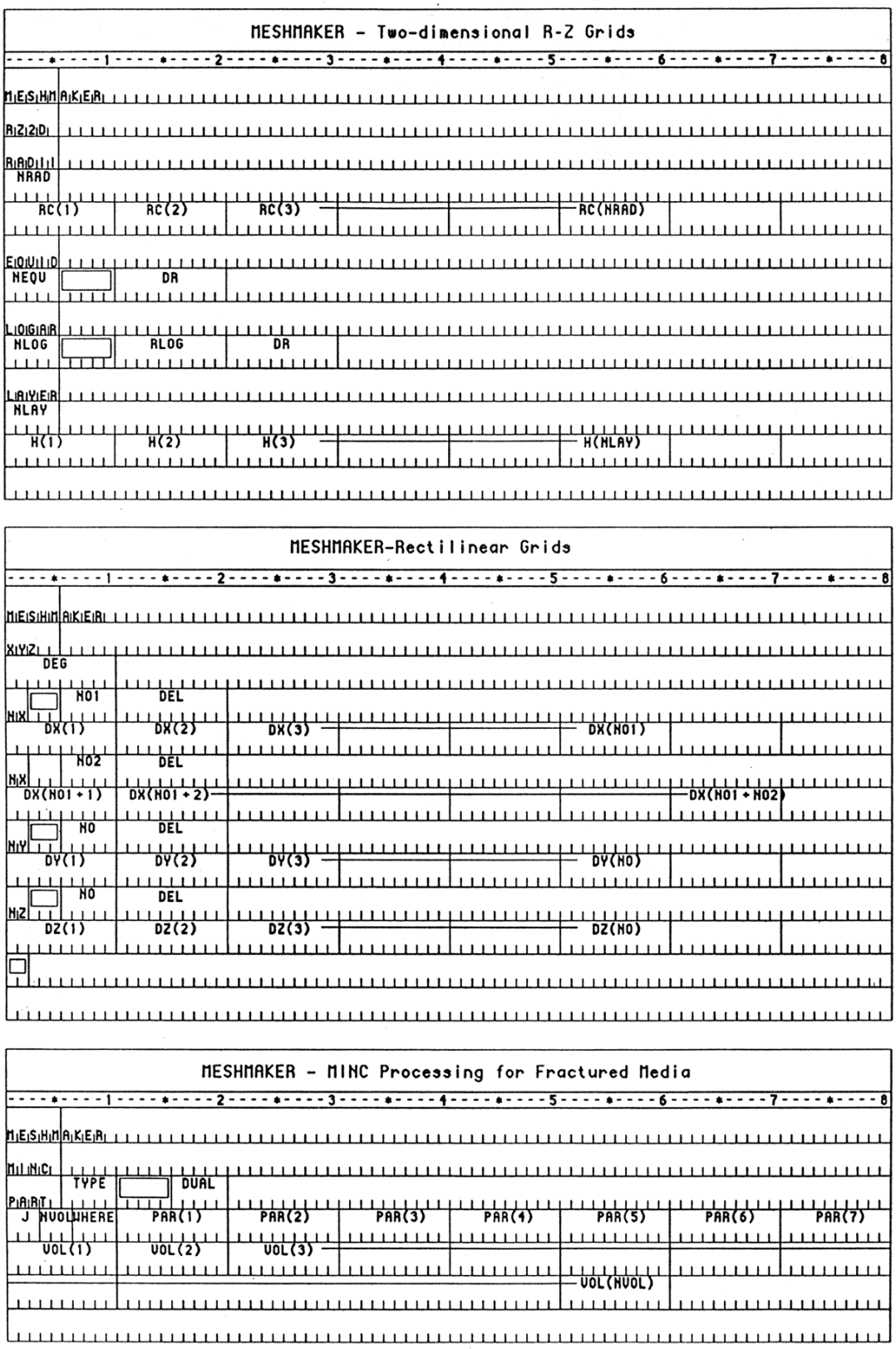


Figure F.1. MESHMaker input formats.

RADII is the first keyword following RZ2D; it introduces data for defining a set of interfaces (grid block boundaries) in the radial direction.

Record RADII.l

Format(I5)
NRAD

NRAD number of radius data that will be read. At least one radius must be provided, indicating the inner boundary of the mesh.

Record RADII.2, RADII.3, etc.

Format(8E10.4)
RC(I), I = 1, NRAD

RC(I) a set of radii in ascending order.

EQUIDistant introduces data on a set of equal radial increments.

Record EQUID. l

Format(I5, 5X, E10.4)
NEQU, DR

NEQU number of desired radial increments.
DR magnitude of radial increment.

Note: At least one radius must have been defined via block RADII before EQUID can be invoked.

LOGARithmic introduces data on radial increments that increase from one to the next by the same factor ($\Delta R_{n+l} = f \bullet \Delta R_n$).

Record LOGAR. l

Format(A5, 5X, 2E10.4)
NLOG, RLOG, DR

NLOG number of additional interface radii desired.
RLOG desired radius of the last (largest) of these radii.
DR reference radial increment: the first ΔR generated will be equal to f • DR, with f internally determined such that the last increment will bring total radius to RLOG. f < 1 for decreasing radial increments is permissible. If DR is set equal to zero, or left blank, the last increment DR generated before keyword LOGAR will be used as default.

Additional blocks RADII, EQUID, and LOGAR can be specified in arbitrary order.

Note: At least one radius must have been defined before LOGAR can be invoked. If DR = 0, at least two radii must have been defined.

LAYER introduces information on horizontal layers, and signals closure of RZ2D input data.

Record LAYER.1

Format(I5)
NLAY

NLAY number of horizontal grid layers.

Record LAYER.2

Format(8E10.4)
H(I), I = 1, NLAY

H(I) a set of layer thicknesses, from top layer downward. By default, zero or blank entries for layer thickness will result in assignment of the last preceding non-zero entry. Assignment of a zero layer thickness, as needed for inactive layers, can be accomplished by specifying a negative value.

The LAYER data close the RZ2D data block. Note that one blank record must follow to indicate termination of the MESHM data block. Alternatively, keyword MINC can appear to invoke MINC-processing for fractured media (see below).

Generation of rectilinear grids

XYZ invokes generation of a Cartesian (rectilinear) mesh.

Record XYZ.1

Format(E10.4)
DEG

DEG angle (in degrees) between the Y-axis and the horizontal. If gravitational acceleration (parameter GF in record PARAM.2) is specified positive, -90° < DEG < 90° corresponds to grid layers going from top down. Grids can be specified from bottom layer up by setting GF or BETA negative. Default (DEG = 0) corresponds to horizontal Y- and vertical Z-axis. X-axis is always horizontal.

Record XYZ.2

Format(A2, 3X, I5, E10.4)
NTYPE, NO, DEL

NTYPE set equal to NX, NY or NZ for specifying grid increments in X, Y, or Z direction.

NO number of grid increments desired.

DEL constant grid increment for NO grid blocks, if set to a non zero value.

Record XYZ.3 (optional, DEL = 0. or blank only)

Format(8E10.4)
DEL(I), I = 1, NO

DEL(I) a set of grid increments in the direction specified by NTYPE in record XYZ.2. Additional records with formats as XYZ.2 and XYZ.3 can be provided, with X, Y, and Z-data in arbitrary order.

Record XYZ.4 a blank record closes the XYZ data block.

Note that the end of block MESHMaker is also marked by a blank record. Thus, when MESHMaker/XYZ is used, there will be two blank records at the end of the corresponding input data block.

MINC processing for fractured media

MINC invokes postprocessing of a primary porous medium mesh from file MESH. The input formats in data block MINC are identical to those of the GMINC program (Pruess, 1983), with two enhancements: there is an additional facility for specifying global matrix-matrix connections ("dual permeability"); further, only active elements will be subjected to MINC-processing, the remainder of the MESH remaining unaltered as porous medium grid blocks. See Appendix C for further discussion.

PART is the first keyword following MINC; it will be followed on the same line by parameters TYPE and DUAL with information on the nature of fracture distributions and matrix-matrix connections.

Format(2A5, 5X, A5)
PART, TYPE, DUAL

PART identifier of data block with partitioning parameters for secondary mesh.

TYPE a five-character word for selecting one of the six different proximity functions provided in MINC (Pruess, 1983b).

ONE-D: a set of plane parallel infinite fractures with matrix block thickness between neighboring fractures equal to PAR(l).

TWO-D: two sets of plane parallel infinite fractures, with arbitrary angle between them. Matrix block thickness is PAR(l) for the first set, and PAR(2) for the second set. If PAR(2) is not specified explicitly, it will be set equal to PAR(l).

THRED: three sets of plane parallel infinite fractures at right angles, with matrix block dimensions of PAR(l), PAR(2), and PAR(3), respectively. If PAR(2) and/or PAR(3) are not explicitly specified, they will be set equal to PAR(l) and/or PAR(2), respectively.

STANA: average proximity function for rock loading of Stanford large reservoir model (Lam et al., 1988).

STANB: proximity function for the five bottom layers of Stanford large reservoir model.

STANT: proximity function for top layer of Stanford large reservoir model.

Note: a user wishing to employ a different proximity function than provided in MINC needs to replace the function subprogram PROX(x) in file meshm.f with a routine of the form:

```
FUNCTION PROX(x)
PROX = (arithmetic expression in x)
RETURN
END
```

It is necessary that PROX(x) is defined even when x exceeds the maximum possible distance from the fractures, and that PROX = 1 in this case. Also, when the user supplies his/her own proximity function subprogram, the parameter TYPE has to be chosen equal to ONE-D, TWO-D, or THRED, depending on the dimensionality of the proximity function. This will assure proper definition of innermost nodal distance (Pruess, 1983b).

DUAL is a five-character word for selecting the treatment of global matrix-matrix flow.

blank: (default) global flow occurs only through the fracture continuum, while rock matrix and fractures interact locally by means of interporosity flow ("double-porosity" model).

MMVER: global matrix-matrix flow is permitted only in the vertical; otherwise like the double-porosity model; for internal consistency this choice should only be made for flow systems with one or two predominantly vertical fracture sets.

MMALL: global matrix-matrix flow in all directions; for internal consistency only two continua, representing matrix and fractures, should be specified ("dual-permeability").

Record PART.l

Format (2I3, A4, 7E10.4)
J, NVOL, WHERE, (PAR(I), I = 1, 7)

J total number of multiple interacting continua (J < 36).

NVOL total number of explicitly provided volume fractions (NVOL < J). If NVOL < J, the volume fractions with indices NVOL+l, ..., J will be internally generated; all being equal and chosen such as to yield proper normalization to 1.

WHERE specifies whether the sequentially specified volume fractions begin with the fractures (WHERE = 'OUT ') or in the interior of the matrix blocks (WHERE = 'IN ').

PAR(I), I = 1, 7 holds parameters for fracture spacing (see above).

Record PART.2.1, 2.2, etc.

Format (8E10.4)
(VOL(I), I = 1, NVOL)

VOL(I) volume fraction (between 0 and 1) of continuum with index I (for WHERE = 'OUT ') or index J+ l - I (for WHERE = 'IN '). NVOL volume fractions will be read. For WHERE = 'OUT ', I = 1 is the fracture continuum, I = 2 is the matrix continuum closest to the fractures, I = 3 is the matrix continuum adjacent to I = 2, etc. The sum of all volume fractions must not exceed 1.

Appendix G. Relative Permeability Functions

Several relative permeability functions are provided in TMVOC for problems involving three-phase water-air-NAPL flow. Unless it is otherwise stated, the original TOUGH2 two-phase functions have been retained. If one of the TOUGH2 two-phase functions is chosen, the NAPL relative permeability will be assumed to be equal to zero. The notation used below is: k_{rw} - aqueous phase relative permeability; k_{rg} - gas phase relative permeability; k_{rn} - NAPL relative permeability. S_g, S_w, and $S_n = 1 - S_g - S_w$ are the saturations of gas, aqueous, and NAPL phases, respectively.

IRP = 5 "All perfectly mobile"

$k_{rg} = 1$
$k_{rw} = 1$
$k_{rn} = 1$
no parameters.

IRP = 6 Modified version of Stone's first three-phase method (Stone, 1970).

$$k_{rg} = \left[\frac{S_g - S_{gr}}{1 - S_{wr}}\right]^n$$

$$k_{rw} = \left[\frac{S_w - S_{wr}}{1 - S_{wr}}\right]^n$$

$$k_{rn} = \left[\frac{1 - S_g - S_w - S_{nr}}{1 - S_g - S_{wr} - S_{nr}}\right]\left[\frac{1 - S_{wr} - S_{nr}}{1 - S_w - S_{nr}}\right]\left[\frac{\left(1 - S_g - S_{wr} - S_{nr}\right)\left(1 - S_w\right)}{\left(1 - S_{wr}\right)}\right]^n$$

When $S_n = 1 - S_g - S_w$ is near irreducible NAPL saturation, $S_{nr} \le S_n \le S_{nr} + .005$, NAPL relative permeability is taken to be

$$k'_{rn} = k_{rn} \cdot \frac{S_n - S_{nr}}{.005}$$

Parameters are S_{wr} = RP(1), S_{nr} = RP(2), S_{gr} = RP(3), n = RP(4).

IRP = 9 three-phase functions of Parker et al. (1987).

$m = 1 - 1/n$

$\bar{S}_g = S_g / (1 - S_m)$

$\bar{S}_w = (S_w - S_m) / (1 - S_m)$

$\bar{S}_l = (S_w + S_n - S_m) / (1 - S_m)$

$$k_{rg} = \sqrt{\bar{S}_g}\,[1 - (\bar{S}_l)^{1/m}]^{2m}$$

$$k_{rw} = \sqrt{\bar{S}_w}\left\{1 - \left[1 - (\bar{S}_w)^{1/m}\right]^m\right\}^2$$

$$k_{rn} = \sqrt{\bar{S}_l - \bar{S}_w}\left\{\left[1 - (\bar{S}_w)^{1/m}\right]^m - \left[1 - (\bar{S}_l)^{1/m}\right]^m\right\}^2$$

where k_{rw}, k_{rg}, and k_{rn} are limited to values between 0 and 1, with S_m =RP(1), and n =RP(2).

IRP = 10 same as IRP = 6 except that

$$k_{rg} = 1 - \left[\frac{S_n + S_w - S_{wr}}{1 - S_{wr}}\right]^n$$

IRP = 11 functions used by Faust (1985) for two-phase Buckley-Leverett problem

$k_{rw} = (S_w - 0.16)^2/0.64$

$k_{rg} = 0$

$k_{rn} = (0.8 - S_w)^2/0.64$

where k_{rw} and k_{rn} are limited to values between 0 and 1, no parameters.

The relative permeability functions listed above should be considered preliminary. TMVOC users are encouraged to follow ongoing research into three-phase relative permeabilities, and to add suitable formulations into subroutine RELP.

This routine has the following structure:

```
      SUBROUTINE RELP(SL,SG,REPL,REPG,REPO,NMAT)
C
      ...
      ...
      ...
C
      GOTO (10,11,12, ...),IRP(NMAT)
C
      ...
      ...
C
   10 CONTINUE                                    | (IRP = 1) |
      ...                                         |           |
      ...                                         |           |
      ...                                         |           |
      REPL= ...                                   |           |
      REPG= ...                                   |           |
      REPO= ...                                   |           |
      RETURN                                      |           |
C
   11 CONTINUE                                    | (IRP = 2) |
      ...                                         |           |
      ...                                         |           |
      ...                                         |           |
      REPL= ...                                   |           |
      REPG= ...                                   |           |
      REPO= ...                                   |           |
      RETURN                                      |           |
C
    12 CONTINUE
      ...
      ...
      ...
C
      END
```

Here, `SL` and `SG` are the aqueous and gas phase saturations (note that for NAPL saturation we have `SO = 1 - SL - SG`). `REPL`, `REPG`, and `REPO` are, respectively, the relative permeabilities of aqueous, gas, and NAPL phases. `NMAT` is the index of the domain to which the grid block belongs, and `IRP(NMAT)` is the index number of the relative permeability function in that domain.

To code an additional relative permeability function, the user needs to insert a code segment analogous to those shown above, beginning with a statement number that would also appear in the `GOTO` statement. The relative permeabilities `REPL`, `REPG`, and `REPO` need to be defined as functions of the phase saturations. The `RP( )` data read in the input file can be utilized as parameters in these functional relationships.

Appendix H. Capillary Pressure Functions

A three-phase capillary pressure function has been included in TMVOC. The original TOUGH2 two-phase functions have been retained, and if one of the TOUGH2 two phase functions is chosen, the gas-NAPL capillary pressure will be assumed to be equal to zero. The notation used below is: P_{cgn} = gas-NAPL capillary pressure; P_{cgw} = gas-water capillary pressure. It should be noted that the capillary pressure between the NAPL and the aqueous phases, P_{cnw} , is given by $P_{cnw} = P_{cgw} - P_{cgn}$.

ICP = 8 three-phase capillary functions from Parker et al. (1987).

$m = 1 - 1/n$

$$\bar{S}_w = (S_w - S_m) / (1 - S_m)$$

$$\bar{S}_l = (S_w + S_n - S_m) / (1 - S_m)$$

$$P_{cgn} = -\frac{\rho_w g}{\alpha_{gn}} [(\bar{S}_l)^{-1/m} - 1]^{1/n}$$

$$P_{cgw} = -\frac{\rho_w g}{\alpha_{nw}} [(\bar{S}_w)^{-1/m} - 1]^{1/n} - \frac{\rho_w g}{\alpha_{gn}} [(\bar{S}_l)^{-1/m} - 1]^{1/n}$$

where S_m = CP(1); n = CP(2); α_{gn} = CP(3); α_{nw} = CP(4).

These functions have been modified so that the capillary pressures remain finite at low aqueous saturations. This is done by calculating the slope of the capillary pressure functions at $\bar{S}_w$ and $\bar{S}_l$ = 0.1. If $\bar{S}_w$ or $\bar{S}_l$ is less than 0.1, the capillary pressures are calculated as linear functions in this region with slopes equal to those calculated at scaled saturations of 0.1.

ICP = 9 zero capillary pressures

$P_{cgn} = 0$

$P_{cgw} = 0$

no parameters.

Additional capillary pressure functions can be programmed into subroutine PCAP in a fashion completely analogous to that for relative permeabilities (see Appendix G).

Subject Index

A

Accumulation terms 21, 29, 31, 58, 133f., 138, 147, 155
Accuracy 6, 13, 19, 49, 52, 58, 73, 139
Acentric factor 11, 15, 151
Acetylene 5, 13, 153
Active blocks 42, 46, 176
Activity coefficients 8f., 13
Adsorption 5, 6, 18, 147
Advection 1, 67, 112, 134, 143
Air 5, 9, 13, 44, 46, 63, 67, 71, 73, 85, 96f., 111, 127, 146, 150, 153f., 162, 165
Air extraction 44
Airflooding 96, 107
Algebraic equations 137
Ambient 110, 127
Analytical solutions 19f.
Aqueous 5, 6, 7, 9, 13, 14, 18, 26, 29, 67, 71, 72, 85, 86, 111ff., 122, 125ff., 133, 143, 145, 146, 153, 162, 179
Aquifer 108f., 112
Architecture 2, 20
Area 139
Arrays 4, 5, 20f., 23, 28f., 31f., 36, 39f., 55
Atmospheric 108ff.
Average 136, 139
Automatic time stepping 19, 22, 157, 159, 160

B

Balance equations 3, 4, 19, 2ff., 2ff., 35, 46, 72, 133ff., 147, 154
Balances (inventory) 55, 86, 97
Benchmark 1, 58
Benzene 67, 85f., 91
Bi-conjugate gradients 52ff., 158
Binary interaction parameters 11f.
Biodegradation 1, 5, 18, 153
Black body 168
Boiling 5, 16
  point 151
Boundary conditions 34, 42, 44f., 67, 71, 96f., 108ff., 172
  Dirichlet 42, 45
  Neumann 45
  no flow 45
  time-dependent 45f.
Buckley-Leverett 63, 180
Bugs (in program) 20

C

Calling sequence 86, 95
Cancellation, numerical 58
Capillary 44, 96f., 109
  effects 6, 9
  fringe 145
  pressure 5, 24, 34, 46, 51, 71, 96, 110, 134, 149f., 161, 166, 167, 182
Caprock 49
Carbon 18, 150, 153
Cartesian (see Grid)
Cartesian coordinates 167
CH4 153
Chemical potential 7f.
Chemicals (see VOCs)
  organic 5
CHEMP (keyword) 150
CO2 5, 13, 153
Code installation 1, 3, 58
COFT (keyword) 35, 164
Comments 36
COMMON blocks 21, 32f.
Compilation 3, 4, 32
Components 5, 7ff., 20, 23ff. 29, 31, 47f., 54f., 58, 60, 67, 71, 73, 85f., 96, 111f., 127, 133ff., 138, 143ff., 150, 154, 161, 165, 169

Composition (phases) 5ff., 9ff., 21, 26f., 44, 47, 96f., 112, 127, 133, 141, 156, 160, 162f.
Compressibility 6, 10, 14, 16, 57, 140, 149
  critical 151
Computational work 46, 52
Computer hardware 3
Concentration 9, 13, 34, 73, 97f., 112f., 143, 154
Condensation 5, 9, 72
Conduction (heat) 6, 49, 134
Conductive layer 49
Confining beds 49f, 157, 167
Conjugate gradient solvers 3, 19, 32f., 52ff., 138, 158
CONNE (keyword) 168, 171
Connections (interfaces) 4, 33ff., 40, 45f., 57, 97, 141, 164, 168, 176
Conservation 145
Constitutive relations 34
Contamination 8, 60, 110, 113, 138, 154
Continuation run (see Restarting)
Continuum 43, 136, 140ff., 177f.
Convection 6, 134
Convergence 19, 21f., 52, 54, 73, 112, 127, 155, 157, 159
  check 22, 138
  criterion 22, 54, 159
  flag 21f., 56
  rate...19, 52, 73
  tolerance 22, 32, 58, 138
Coordinates 19, 42, 139, 167
  global 19, 139f.
Corresponding states 6, 12
Critical
  pressure 10
  properties 6
  temperature 9f., 15f.
Cross-referencing 36
Cylindrical geometry 47

D

Darcy's law 5, 134
Darcy velocity 72, 85, 134
Data
  blocks 34, 35f., 40, 146, 148ff.
  files 34
  geometry 34, 36, 39, 40ff., 51, 136, 148, 172ff.
Decay 5, 18, 153
Defaults 36, 44, 52ff., 63, 138, 147, 149, 153ff., 160, 162
Deliverability (well) 47ff., 71, 112, 169f.
Density 6, 10, 13f., 15f., 18, 48, 85, 112, 133, 149, 152, 157
Departure enthalpy 11, 17
Derivatives, numerical 29, 31, 160
Desorption 6
Differentiation 138
DIFFU (keyword) 165
Diffusion 1, 67, 135
  binary 149
  coefficient 144, 146, 158, 165
  of gases 146, 158
  molecular 5, 60, 96, 112, 143
  multicomponent 111
  multiphase 143ff.
  vapor 112, 143, 158
Diffusive flux 55, 135, 137, 143ff., 158
Diffusivity
  binary 152
  effective 143, 145, 158
  molecular 6, 67, 111
  pressure 140
  thermal 50, 67
Dimensionality (of flow problem) 139
Dimensioning (of arrays) 4, 5, 21, 32f.
Dipole moment 151
Direct solvers (linear equations) 52ff., 158
Dirichlet boundary conditions 42, 45
Discretization 19, 135ff., 145ff.
Disk files 21, 35f., 39, 55, 148
Dispersion 5, 157f.
Dissolution 5, 6, 13f., 72f., 112f., 145
Distribution coefficient 8, 18, 133
Domain 43f., 50f., 109f., 162, 167, 181
Double porosity 19, 140ff., 177
Double precision 3
Drainage 112
Dual permeability 142, 176f.

Duplicate names (of subroutines) 4
Dusty gas 143

E

Electric resistance heating 127
ELEME (keyword) 167
Elements (see Volume elements)
Elevation 109ff.
ENDCY (keyword) 170
ENDFI (keyword) 148
Energy
  balances 19, 23, 29ff., 72, 133f.
  internal 134
  rate 175
Enhanced vapor diffusion 147, 158
Enthalpy 6, 11, 13f., 16f., 47, 71, 111, 134, 156, 159, 170
EOS module 20, 29, 55
Equations (see Balance, Energy, Governing, Mass)
Equation(s)
  algebraic 19, 137
  continuum 136
  cubic 10
  differential 137
  energy 154
  governing 20, 29, 133
  linear 19, 52ff.
  of state 8, 10, 156
  partial differential 135
  steam table 13
EQUID (keyword) 174
Equilibrium 5, 10, 109
  constants 8
  local 23
  gas-static 96
  gravity-capillary 44, 109
  sorption 133
  thermodynamic 139
Error 4, 18, 32, 58
  absolute 159
  duplicate names 4
  relative 159
Ethane 5, 9, 13, 153
Ethylene 5, 13, 153
Evaporation 5
Execution (of program) 3, 20, 22, 86, 95
Expansivity 6, 149
Extensive quantity 136
Extraction 44, 72, 108f., 112f., 125

F

Failure (of a time step) 22, 52
Fickian model 5
Fick's law 143
Field observations 20, 58
Finite differences 19, 50, 135, 137, 139
Finite elements 135
First order 137f.
Floating point 58, 73, 160, 164
Flow
  global 140, 142
  interporosity 140
  rates 156
  steady 109f.
  terms 21, 31f., 155
Fluid
  flow 19
  properties 5ff.
Flux 45, 55, 133ff.
  conservation 145
  diffusive 143ff.
FOFT (keyword) 163
Formats
  data blocks 36
  disk files 36, 40, 42
  input 22, 34, 37ff., 43, 53, 58, 148ff.
FORTRAN 3, 127
Fracture 176f.
  -matrix 145
  spacing 178
Fractured media 19, 40ff., 139ff.
Front 72, 86
Fugacity 8f.

G

Gas 1, 6ff.
  constant 10
  diffusion 67, 112, 143ff.

ideal 11f., 16, 46, 72, 151, 165
non-condensible 1, 5ff., 25, 153
real 8ff.
static 96
thermophysical properties 10ff.
Gauss' divergence theorem 135
GENER (keyword) 169, 171
Generation (see Sinks/sources)
Geometry 19, 34, 36, 39, 136, 139
data 40ff., 51, 136, 148
Geostatistical 51
Geothermal 49
Gibbs' phase rule 23
GMINC program 176
GOFT (keyword) 164
Governing equations 20, 29, 133
Gradient (see also Conjugate gradient) 97, 140f., 143, 145, 172
Gravity 5, 48, 96f., 112, 134, 137, 139, 159, 172, 175
Gravity-capillary equilibrium 44
Grid (see also MESH) 21, 49
block 4, 19f., 23, 26, 28ff., 35, 40, 42f., 44ff., 51ff., 58, 67, 71f., 85f., 91, 96f., 109ff., 127, 137, 139, 141ff., 154f., 157, 160, 162f., 167f., 172, 174ff., 181
block names 42
Cartesian 40, 48, 109f., 175
generation 34, 109f.
increments 174ff.
irregular 19, 40, 139
layers 174f.
nested 141
primary 40, 43, 141, 172, 176
radial 40, 174
Groundwater 44

H

Half life 5, 18, 153
Hardware 3
Harmonic (see Weighting)
Heat 133f.
capacity 12, 50, 151
conduction 49f., 149
conductivity 156
convection 6
exchange 30, 39, 45f., 49f., 140, 157, 167
flow 19, 55, 140
generation 169
latent 6
sensible 6
sink/source 47
specific 50, 97, 134, 149
transfer 6, 134, 168
Henry's
coefficient 6, 10, 13, 15, 154, 165
law 10, 13, 15
Heterogeneity 5, 51, 167
Higher-order methods 40
Homepage (TOUGH2) 1
Homogeneous 110
Hydrocarbons 7ff., 111, 161
Hydrodynamic
dispersion 5
Hydrostatic 44

I

IBM 3, 58
Ideal gas (see Gas, ideal)
IFD (see Integral finite differences)
Impermeable 50
Implicit time differencing 137
Inactive blocks 42, 44f., 46, 50, 67, 110, 172, 175
INCLUDE (file) 4, 32
INCON (keyword) 163, 171
Increments 29, 32, 160, 162, 174ff.
INDOM (keyword) 162
Infiltration 108, 110f., 145
Initial conditions 34ff., 44f., 50, 71f., 85, 96f., 107ff., 127, 154f., 160ff.
Initialization 21, 26f., 36, 60, 109ff., 154f., 160ff.
Injection 24, 47, 71ff., 85, 96f., 111, 141, 170
Input
data 21f., 34ff., 40ff., 55, 58ff., 109ff., 127

formats 22, 34, 37f., 148ff.
Installation (of code) 3, 58
Integral finite differences (IFD) 19, 40, 45, 136ff.
Integration 133
Interface (also see Connection) 19, 33, 50, 139f., 142, 145, 156f., 159, 167f., 174
International Formulation Committee 6
Internet (see Web)
Interphase mass transfer (see Phase partitioning)
Interpolation 21, 47, 137, 156
Interporosity flow 140, 142, 177
Inventory 85, 112f.
Inward unit normal 133, 136
Irreducible (see Saturation)
Isothermal 23, 30, 71, 140
Iteration 19, 21, 29, 45, 52ff., 112, 137f., 155
Iterative solvers (linear equations) 52ff.

J

Jacobian matrix 22, 29ff., 52ff., 73, 138, 157

K

Keywords 34, 58, 148
Klinkenberg parameter 135, 150
Knudsen diffusion 143

L

Laboratory experiments 20, 45, 58, 71, 85, 96
Land surface 108, 111f.
LAYER (keyword) 174
Linear
equations 19, 22, 30ff., 52ff., 73, 156
solvers 52ff., 158
Linking 3, 32
Liquid 24
LOGAR (keyword) 174
LU-factorization 52f., 158

M

MA28 3, 33, 53, 157ff.
Mass 133
balances 19, 23, 29ff., 133ff., 147
component 133, 154
exchange 5, 46, 140, 157
flux 134
fraction 14, 86, 111f., 119, 125f., 133
injection 47, 170
production 169
flow rate 55
transport 135, 143
Matrix (Jacobian) 22, 30ff., 52, 97, 157
Matrix blocks 140f., 176
Memory requirements 4, 52
MESH (see also Grid) 20f.
Cartesian 40, 48, 109, 172, 175f.
file 39ff.
generation 3, 172ff.
primary 176
radial 40, 42, 172ff.
rectilinear 40, 42, 175
MESHM (keyword) 148, 172
Meshmaker 40ff., 172ff.
Methane 5
Metric units 34
Migration (of contaminants) 72
MINC (keyword) 176
MINC (multiple interacting continua) 40ff., 140ff., 176ff.
mixing rules 11
Mixture 1, 7, 8, 12, 14, 49
Mobility 156
Model
mathematical 127
Modular architecture 20
Molar
density 10, 14
enthalpy 16f,
heat capacity 12
units 133
volume 15
weight 46
Mole fraction 8f., 11, 14, 18, 24ff., 34, 47, 60, 72, 86, 97, 133, 144ff.

Molecular diffusion (see Diffusion)
Molecular weight 12, 49, 151
MOP options 155ff.
MULKOM 3
MULTI (keyword) 154
Multiphase 7, 133f., 137, 140, 143ff.
Multiple interacting continua (see MINC)
Multiple porosity 19, 40

N

Naming conventions (for grid blocks) 40, 42f.
NAPL (non-aqueous phase liquid) 1, 5, 6, 9, 13, 15ff., 26, 71ff., 86, 91, 96f., 108, 112f., 126f., 152
  lense 112f.
  redistribution 109, 112, 122
  spill 1, 108f., 111f., 119
Natural state 110, 154
NCG (non-condensible gas) 1, 5ff., 13ff., 24f., 44, 63, 73, 133
NCGAS (keyword) 153
n-decane 67
Neumann boundary conditions 45
Newton-Raphson iteration 7, 26, 29, 31, 52, 55, 73, 112, 137f., 155, 157, 159ff.
Nine-point differencing 40
Nitrogen 73, 97
Nodal
  distance 45, 139, 141, 177
  line 139
  points 42, 110, 137
Non-condensible gas (see NCG)
Nonisothermal 1, 50, 127
Non-linear 137
Nonpolar substance 10
Normal vector 133
NOVER (keyword) 164
n-pentane 112
Numerical
  cancellation 58
  differentiation 29, 138
  performance 58
  roundoff 59
Numerical solution 20

O

Oil (see NAPL)
O-preconditioning 54
Organic carbon 18, 150, 153
Organic chemical (see VOC)
Output 3, 22, 32, 36, 55ff.
Oxygen 73, 97
o-xylene 96, 107

P

PAR array 29
PARAM (keyword) 155
PARAMETER statement 4, 32
Parameters
  computational 34
  hydrogeologic 34
  secondary 20, 28ff., 154
  thermophysical 10ff., 28
PART (keyword) 176
Partial pressure 9
Partial differential equations 19, 135
Partition coefficient 18, 153
Partitioning (among phases) 5, 8ff., 13
PDE (see Partial differential equation)
Peng-Robinson equation of state 11, 165
Permeability 49, 110, 156
  absolute 34, 51, 134, 149, 168
  modification 51, 55
  modifiers 51, 167
  relative 34, 71, 96, 110, 134, 144, 147, 149f., 166, 179f.
  -thickness 47
Petroleum reservoirs 10
Phase (fluid) 5, 20, 127, 133, 154
  aqueous 9, 13ff., 28f., 72, 125, 127
  appearance 5, 7, 19, 23, 26f., 55, 58
  aqueous 122, 133
  boundary 111, 127, 147
  change 7, 127
  composition 21, 26f., 47, 127, 156, 160ff.
  conditions 7, 24
  diagnostic 21

disappearance 5, 7, 19, 23, 26f., 55, 58, 113
distribution 18, 133
equilibria 8
gas 7ff., 28f., 113, 127, 145, 158
index 24ff.
liquid 8f., 16, 145, 158
NAPL 9, 29, 127
oil 13, 144
partitioning 1, 5, 7ff., 13, 60, 127, 143, 145f.
reference 134, 161
single 24, 46, 60, 67, 109, 111, 127, 140
transition 6
three-phase
two-phase 60, 111, 127
Pivoting 54, 157, 159
Plotting 39, 57, 113, 163f., 167
Pore 149
velocity 57, 109
volume 85
Porosity 6, 18f., 34, 51, 110, 133, 149, 163
Porous medium 43, 139, 142, 143, 176
PR (see Peng-Robinson)
Precision (of arithmetic) 3
Preconditioning (linear equations) 3, 52ff., 97, 138, 157f.
Pressure 5, 6, 8, 12, 14f., 24, 45f., 56, 109, 134f., 140f., 146, 162
ambient 110
bottomhole 47f., 56, 169f.
capillary 24, 34f., 46, 51, 56, 71, 96, 110, 134, 149f., 161, 166f., 182
critical 10, 151
diffusivity 140
equilibrium 96, 172
gas 45f.
hydrostatic 44
increase 14
partial 9, 11
reference 16, 134, 161
sandface 112
vapor 8ff., 16f., 26, 97, 151, 158
wellbore 47f., 71
Primary variables 20, 22ff., 28ff., 59, 137, 154, 160ff.
Printout 155, 166
Processes 5
Produced fluid 156
Production 47, 169
rate 48, 170
well 47, 141
Productivity index (PI) 47, 71, 170
Program
execution 3, 20
options 55
structure 3, 20f.
units 3
Proximity function 142, 176f.
Pseudo-component 9
PVT properties 10, 21

Q

Quasi-steady 140

R

Rackett equation 15
RADII (keyword) 174
Radius 174
Radial
flow 47
grid blocks 42
increments 174
symmetry 40, 172
Radiant emittance 168
Radiative heat transfer 134
Random 51, 167
Raoult's law 10
Rate constant 18
Real gas 10
Recharge 108
Records (data) 34, 36, 58, 111, 148ff.
Rectilinear 175
Redlich-Kwong equation of state 10, 72, 165
Relative (see Permeability)
Remediation 1, 44, 108
Reservoir 140
domains 149, 162, 167

Residual 19, 22, 29, 31f., 52, 58, 137f., 160
computation 22
formulation 19
Restarting 44f., 50
Rock 133f.
ROCKS (keyword) 149
Roundoff (numerical) 22, 127
RPCAP (keyword) 166
RZ2D (keyword) 172
RZ2DL (keyword) 172

S

Sample problems 58ff.
Sand 71, 96
Sandstone 45
Saturated 110, 112
Saturated-unsaturated flow 108
Saturated vapor pressure 9, 16f.
Saturation 6, 24ff., 85, 112, 133, 161, 179ff.
irreducible 85, 112, 179
NAPL 113, 122, 126
water 111
Scaling 157
Secondary parameters 20, 28ff., 33, 154
Segment (of a simulation run) 44, 73, 85, 96, 109, 111f.
SELEC (keyword) 164
Semi-analytical 49f.
Seven-point differencing 40
Significant digits 160
Simulation time 111
Single porosity 40
Single precision 3
Sinks/sources 18, 21, 24, 31, 33f., 45ff., 111f., 133, 137, 141, 148, 156f., 164, 169f.
SI units 34
Skin factor 47
Soave-Redlich-Kwong equation of state 10, 11, 72, 165
Soil 144
properties 110
vapor extraction 108f., 112f.
Solid 133
Solubility 6, 13f., 15, 26, 72, 85, 111, 152f., 165
Soluble 144
Solute 67, 143
Solver (linear) 52ff., 97
SOLVR (keyword) 53f., 163
Sorption 1, 18, 133
Source (see Sink)
Space discretization 19, 34, 58, 136ff., 145f.
Sparse matrix 19, 32
Spatial correlation 51, 167
Spill (see NAPL)
SRK (see Soave-Redlich-Kwong)
Stability 19, 137
Standard conditions 146
Standard state 8
START (keyword) 155
Steady (flow, state) 22, 47, 109ff.
Steam
flooding 71ff., 86, 92ff., 127
injection 44, 71ff.
superheated 24
tables 6, 13
Stefan-Boltzmann (law, constant) 134, 168
Step change 85
Step function 156
Storage (see Memory)
Stress 6
Subdomain 133, 141
Subgridding 141f.
Subroutine 1, 4, 21f., 31f., 39, 42, 45, 51, 55, 57, 85, 97, 109, 155, 180ff.
Sun workstation 3
Surface 133, 136
SVE (see Soil vapor extraction)

T

T2DM (dispersion module) 157f.
T2VOC 13, 19, 58, 63, 71ff., 127, 150, 165
-style initial conditions 35, 44, 71, 154, 160ff.
TABLE (disk file) 50
Taylor series 138
TCE 14, 71
Temperature 6, 67, 134, 154, 161, 168

critical 8, 9, 15f., 151
profile 49f.
variation 49f.
Templates 58, 127
Termination (of execution) 22
Text editor 36, 42, 46
Thermal
conductivity 50, 134
diffusivity 50
Thermodynamic
conditions 7, 39, 44f., 72, 111
constraints 60
equilibrium 23, 139
formulation 6ff.
parameters 137
state variables 19ff., 23ff., 28ff., 44f., 55, 160f.
Thermophysical
parameters 20, 22, 31
properties 5ff., 21, 28ff., 34, 52, 71, 150ff.
Three-phase 1, 9, 24, 26, 71, 96, 127, 144, 179ff.
Time
automatic 22
increment 22, 32
discretization 19, 136ff.
series 57, 85, 97, 111ff.
stepping 3, 19, 21f., 34, 44, 52, 55, 58, 86, 111, 127, 138, 155ff., 159, 166
truncation errors 58
TIMES (keyword) 166
Title (data record) 148
Toluene 85f., 91, 96, 107
Tortuosity 111, 143f., 146f., 149
TOUGH 3
TOUGH2 1ff., 6, 19ff., 32, 43, 50, 58, 67, 127, 133, 147f., 158, 164, 179, 182
homepage 1
Tracer 143, 145
Transient 23, 140
Tutorial 58
Two-phase 24, 26

U

Unconfined 108f.
Units
(disk files) 39
matrix 54
metric 150
of measurement 34, 47ff., 133f., 143, 150, 152, 161
of program 1, 3f., 20, 32, 35, 39. 86, 95, 164
SI 34
Unix 3
Unsaturated 8, 60, 108ff.
Update
of program modules 1, 3
of thermodynamic conditions 7, 21f., 26, 29
Upstream (see Weighting)
Utility programs 1

V

Vadose zone 1, 113
Validation (of code) 58
Vapor 112
-air mixtures 146
diffusion 112
pressure 9f., 26, 97, 151
pressure lowering 6, 9, 158
water 11
Vaporization 16, 45, 97
Variables
primary 20, 23ff., 28f., 44, 137, 154
secondary 20
switching 24
Variably saturated 127, 145
Velocity 55, 72, 85, 109, 143
Verification (of code) 58
Version control 1f., 86, 95, 164
Vertical section 108
Viscosity 6, 12f., 14, 17, 134, 152
VOCs (volatile organic chemicals) 1, 5, 6, 8, 9, 12ff., 15ff., 24ff., 44, 85f., 107, 111f., 119, 122, 125ff., 133, 150
adsorbed 150

dissolved 13f.
Volatile 5, 111f., 127, 144
Volume 133, 139, 142
active 42, 46
average 136
elements (see also Grid blocks) 33, 40, 44f., 50, 137, 163f., 167ff.
inactive 42, 46
names 40, 42

W

Wagner equation 17
Water 5ff., 13ff., 85, 111ff.
flooding 71ff., 85, 91
injection 72
saturation 111
table 108ff., 111ff.
vapor 11f.
Web (Internet) 1
Weighting 160
harmonic 137, 145ff., 156, 158, 165
interface 137
upstream 137, 156f., 159
Well 169f.
extraction 108
injection 141
production 47, 141
radius 47
Wellbore 48
pressure 48, 71
Workstation 3

X

Xylene 96
XYZ (keyword) 175

Z

Z-preconditioning 53f.