

EOS7CA Version 1.0:
TOUGH2 Module for Gas Migration in
Shallow Subsurface Porous Media Systems

Curtis M. Oldenburg

Earth Sciences Division
Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

March 6, 2015

This work was carried out as part of the Zero Emissions Research and Technology project funded by the Assistant Secretary for Fossil Energy, Office of Coal and Power Systems through the National Energy Technology Laboratory, and by Lawrence Berkeley National Laboratory under Department of Energy Contract No. DE-AC02-05CH11231.

This page left intentionally blank.

Abstract

EOS7CA is a TOUGH2 module for mixtures of a non-condensable gas (NCG) and air with or without a gas tracer, an aqueous phase, and water vapor. The user can select the NCG as being CO₂, N₂, or CH₄. EOS7CA uses a cubic equation of state with a multiphase version of Darcy's Law to model flow and transport of gas and aqueous phase mixtures over a range of pressures and temperatures appropriate to shallow subsurface porous media systems. The limitation to shallow systems arises from the use of Henry's Law for gas solubility which is appropriate for low pressures but begins to over-predict solubility starting at pressures greater than approximately 1 MPa (10 bar). The components modeled in EOS7CA are water, brine, NCG, gas tracer, air, and optional heat. The real gas properties module (ZEVCA) has options for Peng-Robinson, Redlich-Kwong, or Soave-Redlich-Kwong equations of state to calculate gas mixture density, enthalpy departure, and viscosity. Transport of the gaseous and dissolved components is by advection and Fickian molecular diffusion. This user guide provides instructions for use and two sample problems as verification and demonstration of EOS7CA.

This page left intentionally blank.

Contents

1. Introduction.....	9
2. Mathematical Formulation	10
2.1 General.....	10
2.2 Real Gas Mixture Properties.....	11
Density	11
Enthalpy	12
Viscosity	13
Solubility of Gas Mixture Components	13
2.3 Molecular Diffusion.....	14
3. Implementing Real Gas Components	15
4. Using EOS7CA	20
4.1 Compilation of EOS7CA	20
4.2 Input Formats	20
Single-phase conditions	22
Two-phase conditions	22
5. Example Problems	26
5.1 SAM7CA1: Density, Viscosity, and Enthalpy of Real Gas Mixtures	26
5.2 SAM7CA2: CO ₂ Injection into a shallow vadose zone	36
Introduction.....	36
Results and general description of CO ₂ migration.....	37
6. Final Notes	41
Acknowledgments	42
Nomenclature	42
References.....	44

This page left intentionally blank.

List of Figures

Figure 1. Example of self-documenting printout of key parameters in EOS7CA.	17
Figure 1. (continued). Example of self-documenting printout for EOS7CA.	18
Figure 2. Input file for SAM7CA1CO2.	29
Figure 2. (continued). Input file for SAM7CA1CO2.	30
Figure 3. Portions of output file for SAM7CA1CO2 showing results at various conditions.	31
Figure 4. Input file SAM7CA2 for CO2 injection into shallow vadose zone.	38
Figure 5. Portion of output file for the shallow vadose zone problem SAM7CA2.	39
Figure 6. EOS7CA simulation results for the SAM7CA2 vadose zone problem.	40

List of Tables

Table 1. Module progression and enhancement.	10
Table 2. Phases and components in EOS7CA (NCG = non-condensable gas).	11
Table 3. Molecular diffusivities for two phases and five components.	24
Table 4. SAM7CA1 gas mixture conditions. NCG has been selected as CO ₂ , N ₂ , and CH ₄	28
Table 5. Properties of CO ₂ -Air-H ₂ O mixtures at 1 bar and 20 °C.	32
Table 6. Properties of CO ₂ -Air-H ₂ O gas mixtures at 10 bars and 20 °C.	32
Table 7. Properties of N ₂ -Air-H ₂ O mixtures at 1 bar and 20 °C.	33
Table 8. Properties of N ₂ -Air-H ₂ O gas mixtures at 10 bars and 20 °C.	33
Table 9. Properties of CH ₄ -Air-H ₂ O mixtures at 1 bar and 20 °C.	34
Table 10. Properties of CH ₄ -Air-H ₂ O gas mixtures at 10 bars and 20 °C.	34
Table 11. Enthalpy of CO ₂ (J kg ⁻¹) in gas mixture.	35
Table 12. Enthalpy of N ₂ (J kg ⁻¹) in gas mixture.	35
Table 13. Enthalpy of pure CH ₄ (J kg ⁻¹) in gas mixture.	35
Table 14. Properties of the homogeneous vadose zone.	37

This page left intentionally blank.

1. Introduction

The shallow subsurface is potentially vulnerable to impacts from carbon dioxide (CO₂) leakage up wellbores or permeable faults and fractures from geologic carbon sequestration sites. In addition, methane (CH₄) from deep sources or buried pipelines may migrate within the shallow subsurface. The need to evaluate the flow and transport of leaking CO₂ in the shallow subsurface prompted the development of the simulation capabilities provided in TOUGH2/EOS7CA. These capabilities for CO₂ were then extended to include the choice between CO₂, N₂, or CH₄ as the NCG component that is modeled along with air which is always present.

EOS7CA is related to a series of modules derived from the EOS3 module as shown in Table 1. The starting point for development of EOS7CA was the radionuclide transport module EOS7R (Oldenburg and Pruess, 1995; Pruess et al., 1999; 2011), to which we added capabilities for modeling real gas mixtures such as CO₂ and air. This report describes EOS7CA, the TOUGH2 module for simulating CO₂ (or N₂ or CH₄) and air mixing processes in shallow subsurface porous media systems. Applications of early versions of EOS7CA were published in Oldenburg and Unger (2003), Oldenburg et al. (2010a,b), and Lewicki et al. (2009). The sample problems and input format descriptions in the present report along with the TOUGH2 User's Guide (Pruess et al., 1999; 2011) provide sufficient information for using EOS7CA. EOS7C (Oldenburg et al., 2004) is very similar to EOS7CA, except that it models methane (CH₄) instead of air, and it has a solubility model that is accurate for deep (high pressure) systems whereas the solubility model in EOS7CA is limited to shallow (low pressure) systems.

Table 1. Module progression and enhancement.

TOUGH2 Module	Components	Added Capability
EOS3	Water, air, heat	
EOS7	Water, brine, air, heat	Dense brine
EOS7R	Water, brine, parent radionuclide, daughter radionuclide, air, heat	Decay, adsorption, volatilization of radionuclides in trace concentrations.
EOS7CA	Water, brine, NCG (CO ₂ , N ₂ , or CH ₄), gas tracer, air, heat	Real gas mixture properties, solubility model limited to low-pressure systems
EOS7C	Water, brine, CO ₂ (or N ₂), gas tracer, CH ₄ , heat	Real gas mixture properties and accurate solubility model for high-pressure systems

2. Mathematical Formulation

2.1 General

The general conservation equations solved in TOUGH2 for simulating multicomponent and multiphase flow and transport in porous media are presented in Pruess et al. (1999; 2011) along with a complete description of the theory and use of TOUGH2. In this report, we describe EOS7CA and its specific methods and capabilities for modeling two phases and five components plus heat in shallow subsurface systems. Table 2 shows the symbols and index numbers for the phases and components in EOS7CA. The non-condensable gas (NCG) can be chosen by the user as either carbon dioxide (CO₂), nitrogen (N₂), or methane (CH₄) (see input parameter IE(16)). Accurate density, viscosity, and enthalpy of the gas mixtures are included in EOS7CA through the use of a real gas properties module ZEVCA as described below.

Table 2. Phases and components in EOS7CA (NCG = non-condensable gas).

Phases (β)	Components (κ)				
1 – gas (g)	1 – water	2 – brine	3 – NCG	4 – tracer	5 – air
2 – aqueous (w)	1 – water	2 – brine	3 – NCG	4 – tracer	5 – air

2.2 Real Gas Mixture Properties

Density

EOS7CA makes use of a set of subroutines contained within a submodule called ZEVCA where ZEV stands for Z factor, Enthalpy, and Viscosity, and CA indicates use with EOS7CA. These subroutines are independently implemented in WebGasEOS, a publicly available webtool (Reagan, 2006; <http://esdtools.lbl.gov/gaseos/gaseos.html>). ZEVCA calculates properties of real gas mixtures using cubic equations of state, so-named because the volume terms are raised to either the first, second, or third power (Reid et al., 1987). The most common two-parameter equations of state can be written as

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2} \quad (1)$$

where the parameters and functions u , w , b , and a take on different values depending on the particular cubic equation of state being used, and T is in degrees K. Other symbols are defined in Nomenclature. Depending on user input (see input parameter IE(15)), EOS7CA can invoke Peng-Robinson, Redlich-Kwong, or Soave-Redlich-Kwong cubic equations of state. Readers interested in details of equations of state should consult Reid et al. (1987) and Poling et al. (2000) for more information.

The approach taken in EOS7CA is to use the equation of state to calculate the Z factor of the mixture, where

$$PV = Z n R T \quad (2)$$

From this value, the density of the gas mixture can be calculated using

$$\rho = \frac{MW n}{V} = \frac{P MW}{Z R T} \quad (3)$$

where the molecular weight (MW) is the molecular weight of the real gas mixture.

Enthalpy

Real-gas mixtures depart from ideality in ways that can be modeled with cubic equations of state. The enthalpy of the real-gas mixtures is calculated using an ideal gas value with an added enthalpy departure to account for real gas effects. In ZEVCA, we calculate enthalpy as

$$H = (H - H^{ig}) + H^{ig} = (H - H^{ig}) + \sum_i X^i H^{i,ig} \quad (4)$$

where $(H - H^{ig})$ is the enthalpy departure. ZEVCA uses cubic equations of state (e.g., Peng-Robinson) to calculate the enthalpy departures and ideal gas enthalpy change to come up with the total enthalpy change of the real gas mixture.

Standard TOUGH2 (Pruess et al., 1999; 2011) uses real-gas properties (steam tables) for steam enthalpy, and thus produces more accurate steam enthalpies than the cubic equations of state can provide. At user discretion (see input parameter IE(14)), the user can choose to use the steam tables (subroutine SUPST) to calculate the enthalpy of the steam (water vapor) fraction in the gas, and ZEVCA to calculate the enthalpy of the NCG and air mixture fraction. The total gas mixture enthalpy is then calculated as a weighted combination of the SUPST and ZEVCA contributions. The reference state for enthalpy calculations in ZEVCA is normalized to agree with standard TOUGH2 and the NIST Chemistry Web Book (NIST, 2013), i.e., internal energy is zero for saturated liquid at 273.16 K (0.01 °C).

Viscosity

Another important transport property for gas flow and transport is the viscosity of the real gas mixture. ZEVCA uses the method of Chung et al. (1988) as described in Reid et al. (1987) and Poling et al. (2000). This method is accurate to within 5-10% for the range of conditions expected in subsurface natural gas reservoirs.

Solubility of Gas Mixture Components

Solubility of the gas components (*i*) is modeled using Henry's Law, e.g.,

$$P^i = K_h^i x_{aq}^i \quad (5)$$

where K_h^i is generally dependent on temperature. For the NCG component, the partial pressure of the NCG, e.g., P^{CO_2} for CO₂, is related to the mole fraction of CO₂ in the aqueous phase ($x_{aq}^{CO_2}$) by Henry's Law where temperature dependence of K_h is calculated by the models of

Cramer (1982), and D'Amore and Truesdell (1988) similar to the approach of TOUGH2/EWASG (Battistelli et al., 1997). In EOS3, K_h^{air} was approximated as 1.0×10^{10} Pa, i.e., temperature dependence was ignored for the solubility of air in water. In EOS7, salinity-dependence of K_h^{air} was included by increasing K_h^{air} in aqueous solutions with higher brine mass fractions. EOS7CA retains these EOS3 and EOS7 approaches to preserve continuity with EOS3 and EOS7, and extends the methods by assuming for expediency that the same effects of brine on air solubility occur also for NCG and tracer components. For example, if the Henry's Law coefficient for air in pure water and in brine at the local brine concentration are K_{h,H_2O}^{air} and $K_{h,brine}^{air}$, respectively, then the Henry's Law coefficient for NCG in pure water at a given temperature would be multiplied by the ratio $K_{h,brine}^{air} / K_{h,H_2O}^{air}$ to obtain the value for the NCG Henry's Law coefficient at the given brine mass fraction. The Henry's Law approach in EOS7CA is accurate for low-pressure conditions ($P < 10$ bar or 1 MPa), but over predicts solubility at larger pressures.

2.3 Molecular Diffusion

EOS7CA v. 1.0 includes binary diffusion of the chemical components dissolved in aqueous and gas phases as discussed in the TOUGH2 User Guide (Pruess et al., 1999; 2011). TOUGH2 includes pressure and temperature effects on gas-phase diffusion. Specifically, molecular diffusivity is assumed to be inversely proportional to pressure (P) by the factor $1.0 \times 10^5/P$ (Pruess et al., 2011). For example, if pressure is 2×10^5 Pa, the corresponding effective molecular diffusivity for the gas is one-half the input value which is referenced to 1.0×10^5 Pa. This approach over-predicts diffusivity for CO₂ mixtures above approximately 20 bars (Poling et al., 2000, p. 11.16), with a total overprediction of a factor of two at $P = 100$ bars. Temperature

effects on diffusion are also modeled by inclusion of the factor $((T + 273.15)/273.15)^{\text{TEMP}}$ (see TOUGH2 User Guide (Pruess et al., 2011)). If molecular diffusivity is input as a negative number in TOUGH2, the absolute value of this number is used for the phase molecular diffusivity without modification by pressure or temperature or S and τ (saturation and tortuosity) Interested readers are referred to Pruess et al. (2011), Appendix D, for further details.

3. Implementing Real Gas Components

As shown in Table 1, EOS7CA was developed by changing the volatile radionuclide components of EOS7R into a non-condensable gas (NCG) component (CO₂, N₂, or CH₄, as specified by the user through input parameter IE(16)), and a volatile tracer. One mole of air in EOS7CA is treated internally as a mixture of 0.79 moles N₂ and 0.21 moles O₂ for calculation of gas mixture properties in ZEVCA. The properties (density and viscosity) of the whole gas mixture containing potentially water vapor, NCG, and air are calculated using ZEVCA (e.g., with Peng-Robinson equation of state). The solubility of the gas components is modeled using Henry's Law as discussed in Section 2.2.

EOS7CA is designed for two-phase conditions (i.e., gas and aqueous phases present) in the shallow subsurface and very limited testing has been done for single-phase conditions. In two-phase conditions, vapor pressure is independent of salinity of the aqueous phase. As the brine component is nonvolatile, vaporization would tend to increase brine mass fractions in the aqueous phase beyond unity. Users need to be aware of this possibility, which arises from the fact that EOS7CA, like EOS7, represents the aqueous phase as a mixture of water and brine, not as a mixture of water and salt. Therefore, EOS7CA cannot be used for processes in which solubility limits would be reached, at which point solid salt would precipitate. The tracer

component in EOS7CA does not affect gas properties and is expected to exist only in trace concentrations (e.g., mass fractions of order 10^{-6}). A summary of EOS7CA specifications is printed upon execution and is reproduced here in Fig. 1.


```

*****
*          EOS7CA: EQUATION OF STATE FOR MIXTURES OF WATER/BRINE/NON-CONDENSIBLE GAS/TRACER/AIR          *
*****

          EQUATION OF STATE: PR (IE(15) = 1)          NON-CONDENSIBLE GAS: CO2 (IE(16) = 1)

OPTIONS SELECTED ARE: (NK,NEQ,NPH,NB,NKIN) = (5,6,2,8,5)

          NK = 5 - NUMBER OF COMPONENTS
          NEQ = 6 - NUMBER OF EQUATIONS PER GRID BLOCK
          NPH = 2 - NUMBER OF PHASES THAT CAN BE PRESENT
          NB = 8 - NUMBER OF SECONDARY PARAMETERS (OTHER THAN' COMPONENT MASS FRACTIONS)
          NKIN = 5 - number of components for initializing thermodynamic conditions (default is NKIN = NK)

          For NB = 6, diffusion is "off", for NB = 8, diffusion is "on"

AVAILABLE OPTIONS for (NK,NEQ,NPH,NB):
          (5,5,2,6 or 8) - WATER, BRINE, NCG, TRC, AIR; ISOTHERMAL;          VARIABLES (P, XB, XNCG, XTRC, X OR S+10, T)
          (5,6,2,6 or 8) - WATER, BRINE, NCG, TRC, AIR; NON-ISOTHERMAL;          VARIABLES (P, XB, XNCG, XTRC, X OR S+10, T)
          (4,4,2,6 or 8) - WATER, BRINE, NCG, TRC, NO AIR; ISOTHERMAL;          VARIABLES (P, XB, XNCG, XTRC, T)
          (4,5,2,6 or 8) - WATER, BRINE, NCG, TRC, NO AIR; NON-ISOTHERMAL;          VARIABLES (P, XB, XNCG, XTRC, T)

NKIN = NK or NKIN = NK-2. Default options are (5,5,2,8) - isothermal, diffusion "on", NKIN=NK

THE NK = 4 ("NO AIR") OPTIONS MAY ONLY BE USED FOR PROBLEMS WITH SINGLE-PHASE LIQUID CONDITIONS THROUGHOUT.

THE NORMAL NUMBER OF SECONDARY PARAMETERS OTHER THAN MASS FRACTIONS IS 6 PER PHASE. IN EOS7CA, WE OPTIONALLY ADD TO THIS A
SATURATION-DEPENDENT TORTUOSITY FOR EACH PHASE, AS WELL AS TEMPERATURE AND PRESSURE DEPENDENCE OF THE DIFFUSION COEFFICIENT.
*****

          NKIN = 5    *** ALLOWS INITIALIZATION WITH DIFFERENT SETS OF PRIMARY VARIABLES. ***
                    *** THIS IS USEFUL FOR STARTING EOS7CA SIMULATIONS FROM EOS7 INITIAL CONDITIONS. ***
                    = NK (default): (P,XB,XNCG,XTRC,XAIR,T) FOR SINGLE PHASE, (P,XB,XNCG,XTRC,S+10,T) FOR TWO-PHASE. (EOS7CA FORMAT).
                    = NK-2: (P,XB,XAIR,T) FOR SINGLE PHASE, (P,XB,S+10,T) FOR TWO-PHASE. (EOS7 FORMAT). WILL INITIALIZE XNCG = XTRC = 0.

MOP(20) = 0 *** CONTROLS HANDLING OF NEGATIVE AIR MASS FRACTIONS.
          = 0: DO NOT INCREASE PRESSURE TO AVOID NEGATIVE AIR MASS FRACTIONS
          = 1: INCREASE PRESSURE TO AVOID NEGATIVE AIR MASS FRACTIONS

IE(14) = 1 *** CONTROLS CALCULATION OF GAS ENTHALPY
          = 0: USE SUPST FOR VAPOR, ZEVCA FOR NCG AND AIR
          = 1: USE ZEVCA FOR THE WHOLE MIXTURE

*****

```

Figure 1. Self-documenting printout of key parameters for specifying components and phases in EOS7CA.

THE PRIMARY VARIABLES ARE

P - PRESSURE T - TEMPERATURE XB - BRINE MASS FRACTION
 XNCG - MASS FRACTION OF NON-CONDENSIBLE GAS XTRC - MASS FRACTION OF VOLATILE TRACER
 S+10. - (GAS PHASE SATURATION + 10.) X - AIR MASS FRACTION IN GAS T - TEMPERATURE

```

*****
*          COMPONENTS          *
*****
*          # 1 - WATER         *
*          # 2 - BRINE         *
*          # 3 - NCG           *
*          # 4 - TRC           *
*          # 5 - AIR           *
*          # 6 - HEAT          *
*****

*****
*          FLUID PHASE CONDITION          PRIMARY VARIABLES          *
*****
*          SINGLE-PHASE GAS (#)          P, XB, XNCG, XTRC,          X, T *
*          SINGLE-PHASE LIQUID (*)          P, XB, XNCG, XTRC,          X, T *
*          TWO-PHASE (*)          P, XB, XNCG, XTRC, S+10., T *
*****
*          (#) XB, XNCG, XTRC AND X ARE MASS FRACTIONS IN THE GAS PHASE.
*          (*) XB, XNCG, XTRC AND X ARE MASS FRACTIONS IN THE AQUEOUS PHASE.
*****

```

BRINE PROPERTIES

DENSITY = 0.118500E+04 KG/M**3 AT REFERENCE CONDITIONS OF (P,T) = (0.100000E+06 PA,0.200000E+02 DEG-C)
 COEFFICIENTS FOR BRINE VISCOSITY ARE: VCO(I) = 0.481900E+00 -0.277400E+00 0.781400E+00

PROPERTIES OF NCG AND TRACER:	DOMAIN	NCG	TRC
HALF-LIFE (SECONDS):	-ALL-	NO DECAY	0.1000E+51
MOLECULAR WEIGHT (GM/MOLE):	-ALL-	0.4400E+02	0.2300E+03
INVERSE HENRY CONST. (MOLE/PA):	-ALL-	VARIABLE	0.5700E-10
HEAT CAPACITY (J/(KG K)):	-ALL-	0.8240E+03	NEGLIGIBLE
GAS PHASE DIFFUSIVITY (M**2/S):	-ALL-	0.1000E-04	0.1000E-04
AQ. PHASE DIFFUSIVITY (M**2/S):	-ALL-	0.1000E-09	0.1000E-09
DISTRIBUTION COEFF. (M**3/KG):	rock	0.0000E+00	0.0000E+00

MOLECULAR DIFFUSIVITY OF WATER, BRINE, NCG, TRC, AND AIR THROUGH THE GASEOUS AND AQUEOUS PHASES, (FDDIAG(PHASE,COMP)) [M**2/S]:

PHASE 1 = GAS; PHASE 2 = AQUEOUS

PHASE COMP	PHASE COMP	PHASE COMP	PHASE COMP	PHASE COMP	PHASE COMP	PHASE COMP	PHASE COMP	PHASE COMP	PHASE COMP	PHASE COMP									
-1-	-1-	-1-	-2-	-1-	-3-	-1-	-4-	-1-	-5-	-2-	-1-	-2-	-2-	-2-	-3-	-2-	-4-	-2-	-5-
0.10000E-04	0.00000E+00	0.10000E-04	0.10000E-04	0.10000E-04	0.10000E-04	0.10000E-09	0.00000E+00	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09	0.10000E-09

Figure 1. (continued). Example of self-documenting printout for EOS7CA.

4. Using EOS7CA

4.1 *Compilation of EOS7CA*

As an extension of TOUGH2, EOS7CA consists of all of the TOUGH2 V2.1 subroutines and the new equation of state module EOS7CA subroutines and ZEVCA subroutines. Typical compilation on a LINUX workstation with the Portland Group Fortran compiler, for example, would be as follows:

```
pgf77 -c -r8 -i8 t2fm.f t2cg22.f t2f.f t2solv.f meshm.f eos7cav1.f zevcav1.f
```

```
pgf77 -o x7ca t2fm.o t2cg22.o t2f.o t2solv.o meshm.o eos7cav1.o zevcav1.o
```

A GFortran Makefile is as follows:

```
#Makefile
objects = t2fm.o t2cg22.o t2f.o t2solv.o meshm.o eos7cav1.o zevcav1.o
FC = gfortran
FFLAGS = -g -freal-4-real-8 -fno-align-commons -std=legacy

x7ca: $(objects)
    $(FC) -o x7ca $(objects)

%.o: %.f
    $(FC) $(FFLAGS) -c $<
```

The italics indicate the new program units of EOS7CA.

4.2 *Input Formats*

Below we describe the input formats for specifying EOS7CA-specific input. Other TOUGH2 input parameter formats are given in Pruess et al. (2011). EOS7CA-specific input parameters are provided through the MULTI block, SELEC block and PARAM block.

MULTI format(4I5)
 NK, NEQ, NPH, NB, NKIN
 NK Set NK = 5 for water, brine, NCG, gas tracer, and air.
 NEQ Number of equations per grid block.
 Set NEQ = NK for isothermal problems.
 Set NEQ = NK + 1 for nonisothermal problems.
 NPH Number of phases. Set NPH = 2.
 NB Number of secondary parameters. Set NB = 6 for no-diffusion,
 NB = 8 for diffusion on.
 NKIN Number of mass components in INCON (default is NKIN = NK).
 This parameter can be used to initialize EOS7CA run (NK = 4 or
 5) with EOS7 (NK = 2 or 3) INCON data, in which case NCG and
 tracer (components 3 and 4) are initialized with $X_{g,l}^K = 0$.

PARAM.1 format(2I2, 3I4, 24I1, 2E10.4)
 NOITE, KDATA, MCYC, MSEC, MCYPR, (MOP(I), I = 1, 24), DIFF0, TEXP
 See TOUGH2 User Guide (Pruess et al., 1999; 2011) or TOUGH2
 informative printout for description of all of the above parameters
 except the following:

MOP(20) Option for resetting variables.¹
 0: Variables are not reset if partial pressures exceed total pressure.
 1: Pressure is reset to sum of partial pressures if partial pressures
 exceed total pressure.

¹This option is needed because in some cases, the sum of partial pressures exceeds the total pressure, e.g., if temperature changes cause rapid exsolution of dissolved gases. When this occurs, erroneous negative mass fractions can arise. In this case, setting MOP(20) = 1 can alleviate the problem. However, as a default, we recommend setting MOP(20) = 0, as this problem is not often encountered.

PARAM.4 primary variables used for default conditions for all grid blocks that are not

assigned by means of data blocks INDOM or INCON. Option START is necessary to invoke these default initial conditions for grid blocks (for additional information, see the TOUGH2 User Guide description of keyword PARAM.4). Two lines will be read for the six primary variables in EOS7CA. See INCON description for primary variable description.

PARAM.4 format(4E20.14)

DEP(I), I = 1,6

INCON introduces grid block-specific initial conditions. Two lines will be read per grid block for the six primary variables in EOS7CA.

INCON.1 format(4E20.14,/,2E20.4)

DEP(I), I = 1,6

DEP(I) are the primary variables as follows:

Single-phase conditions

$(P, X^{brine}, X^{ncg}, X^{trc}, X^{air}, T)$ where P is pressure, X^{brine} is always brine mass fraction in the liquid phase, other X 's are mass fractions in gas or liquid phase, and T is temperature in °C.

Two-phase conditions

$(P, X^{brine}_{liq}, X^{ncg}_{liq}, X^{trc}_{liq}, S + 10, T)$ where P is gas-phase pressure, X 's are brine, NCG, and TRC mass fractions in the liquid, S is gas saturation, and T is temperature in °C

SELEC keyword to introduce a data block with reference brine and NCG input data.

SELEC.1 format(8I5)

IE(1), NGBINP(1), NGBINP(2), NGBINP(3), NFBL, NFBR, NFBT, NFBB

IE(1) Set equal to 6 to read six additional data records.

IE(14) Set equal to 0 to use ZEVCA for enthalpy of gas mixture,
Set equal to 1 to use SUPST for water vapor, and ZEVCA for
NCG and air, with a weighted sum used for the mixture enthalpy.

IE(15) Set equal to 1 for Peng-Robinson (PR) equation of state;
Set equal to 2 for Redlich-Kwong (RK) equation of state;

IE(16) Set equal to 3 for Soave-Redlich-Kwong (SRK) equation of state.
 Set equal to 1 for NCG = CO₂,
 Set equal to 2 for NCG = N₂,
 Set equal to 3 for NCG = CH₄.

SELEC.2 format(3E10.4) (unchanged from standard EOS7)
 P0, T0, ρ0
 P0 Reference pressure, in Pa
 T0 Reference temperature, in °C
 ρ0 Brine density at (P0, T0), in kg m⁻³.
 For P0, T0, ρ0 equal to zero or blank, default values of P0 = 1 × 10⁵ Pa, T0 = 25 °C, and ρ0 = 1185.1 kg m⁻³ will be used. For P0 < 0, brine will be assumed to be pure water. This allows modeling of flow with two waters that differ only in trace constituents, but have identical thermophysical properties.

SELEC.3 format(3E10.4) (unchanged from standard EOS7)
 v(i), i = 1,3
 v(i) Coefficients for salinity correction in aqueous phase viscosity (see Pruess et al., 1999, p. 41). If v(i) = 0 for i = 1, 2, 3, default values will be used: v(1) = 0.4819, v(2) = -0.2774, v(3) = 0.7814. Specification of brine as pure water in record SELEC.2 will override viscosity specifications and will always result in viscosity of pure water being used.

SELEC.4 format(7E10.4)
 Leave this line blank.

SELEC.5 format(7E10.4)
 Leave this line blank.

SELEC.6 format(7E10.4)

Leave this line blank.

SELEC.7 format(7E10.4)

blank, XMW(4), blank, blank, blank, blank, HCTRC

XMW(4) Molecular weight of tracer component 4, in g/mole.

HCTRC Inverse Henry's constant for gas tracer (component 4), in Pa⁻¹ .

DIFFU format(2E10.4)

FDDIAG(1,1),FDDIAG(2,1)

FDDIAG(1,2),FDDIAG(2,2)

FDDIAG(1,3),FDDIAG(2,3)

FDDIAG(1,4),FDDIAG(2,4)

FDDIAG(1,5),FDDIAG(2,5)

Molecular diffusivity of components 1–5 in phases 1, 2 (gas and liquid) in m² s⁻¹. If FDDIAG(NP,NK) is input as a negative number, the absolute value is used for the phase molecular diffusivity (d_{β}^K) without modification by S and τ (saturation and tortuosity) and without pressure or temperature effects in the case of gas diffusivity.

Table 3. Molecular diffusivities for two phases and five components.

Phase	Component	(NP,NK)	Input	Units
Gaseous	Water	(1,1)	DIFFU(1,1)	m ² s ⁻¹
	Brine	(1,2)	DIFFU(1,2)	m ² s ⁻¹
	NCG	(1,3)	DIFFU(1,3)	m ² s ⁻¹
	Tracer	(1,4)	DIFFU(1,4)	m ² s ⁻¹
	Air	(1,5)	DIFFU(1,5)	m ² s ⁻¹
Aqueous	Water	(2,1)	DIFFU(2,1)	m ² s ⁻¹

	Brine	(2,2)	DIFFU(2,2)	$\text{m}^2 \text{s}^{-1}$
	NCG	(2,3)	DIFFU(2,3)	$\text{m}^2 \text{s}^{-1}$
	Tracer	(2,4)	DIFFU(2,4)	$\text{m}^2 \text{s}^{-1}$
	Air	(2,5)	DIFFU(2,5)	$\text{m}^2 \text{s}^{-1}$

5. Example Problems

5.1 SAM7CA1: Density, Viscosity, and Enthalpy of Real Gas Mixtures

In this section, we present results from a simple test problem designed to demonstrate the gas mixture property calculations of EOS7CA v. 1.0 through comparison of computed properties with independent reference values. The domain consists of six grid blocks arranged in two columns with three rows. The various conditions are shown in Table 4.

The input file for SAM7C1 for NCG = CO₂ is shown in Figure 2. A partial output file is shown in Figure 3. Note the first three letters of the grid block name suggests the compositions in each grid block, while the last two numbers give the row and column, respectively. In Tables 5-13, we present a summary of the results and comparisons to standard reference values.

The first comparison we present is for density (ρ) and viscosity (μ) of the NCG–air mixture at 20 °C and 1 and 10 bars (Tables 5-10). For brevity, we present in Tables 5-10 physical properties only for the end members and 50-50 mole fraction mixtures. We have included reference values either from the NIST Chemistry WebBook (NIST, 2013), or from WebGasEOS (Reagan, 2006). Note that the EOS7CA output file gives compositions in terms of mass fraction (X), whereas the compositions in the tables are specified in terms of mole fractions in the gas (x_g) phase for consistency with the reference sources. The conversions from mass fraction to mole fraction are given by the equations

$$x^i = \frac{X^i}{\sum_i \frac{X^i}{MW^i}} \quad (6)$$

$$X^i = \frac{x^i MW^i}{\sum_i x^i MW^i} \quad (7).$$

Note further in Tables 5-13 that for these two-phase conditions with water present, there is a small amount of water vapor in the gas phase that is not present in the reference calculations. As shown in Tables 5-10 for CO₂, N₂, and CH₄, EOS7CA approximates gas mixture properties very well.

In Tables 11-13, we present comparisons of enthalpy calculations using the IE(14) = 1 option, i.e., SUPST for steam fraction and ZEVCA for CO₂ and air fractions. This approach appears to be acceptable as shown by comparing EOS7CA estimates against NIST Chemistry WebBook values.

Table 4. SAM7CA1 gas mixture conditions. NCG can be selected as CO₂, N₂, or CH₄.

Two-Phase P = 1 bar T = 20 °C	Two-Phase P = 10 bar T = 20 °C
$x_g^{\text{NCG}} = 1.0$ $x_g^{\text{Air}} = 0.0$ $x_g^{\text{H2O}} = \text{trace}$	$x_g^{\text{NCG}} = 1.0$ $x_g^{\text{Air}} = 0.0$ $x_g^{\text{H2O}} = \text{trace}$
$x_g^{\text{NCG}} = 0.5$ $x_g^{\text{Air}} = 0.5$ $x_g^{\text{H2O}} = \text{trace}$	$x_g^{\text{NCG}} = 0.5$ $x_g^{\text{Air}} = 0.5$ $x_g^{\text{H2O}} = \text{trace}$
$x_g^{\text{NCG}} = 0.0$ $x_g^{\text{Air}} = 1.0$ $x_g^{\text{H2O}} = \text{trace}$	$x_g^{\text{NCG}} = 0.0$ $x_g^{\text{Air}} = 1.0$ $x_g^{\text{H2O}} = \text{trace}$

```

*SAM7CA1CO2* ... Verification problem for EOS7CA.
ROCKS-----1-----2-----3-----4-----5-----6-----7-----8
rock      2      2600.      .20      1.e-12      1.e-12      1.e-12      2.51      1000.
          0.25
          7          0.20          .27          1.          0.01
          7          0.20          .25          .00084          1.e5          1.

MULTI-----1-----2-----3-----4-----5-----6-----7-----8
          5          6          2          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          1          110 090000020000400 3
          -1.          9.8066
          1.e-9
          1.e-5
          1.000e5          0.          0.e-1          0.e-4
          10.500          20.

IE(14) = 1, use SUPST & ZEVCA for enthalpy.      IE(14) = 0, use ZEVCA only.
IE(15) = 1, use Peng-Robinson eqn. of state.      IE(15) = 2,3 use RK,SRK, resp.
IE(16) = 1, 2, or 3 NCG is CO2, N2, or CH4, respectively.
SELEC-----1-----2-----3-----4-----5-----6-----7-----8
          6          1          1          1
          -1.e5

          1.e50      230.00      0.0      0.0      0.0      0.0      5.70e-11

diffusivity data are input as follows:
first row: water (gas, liq.)
second row: brine (gas, liq.)
third row: ncg (gas, liq.)
fourth row: trc (gas, liq.)
fifth row: ch4 (gas, liq.)
DIFFU-----1-----2-----3-----4-----5-----6-----7-----8
          1.e-5      1.e-10
          0.e-6      0.e-6
          1.e-5      1.e-10
          1.e-5      1.e-10
          1.e-5      1.e-10

```

Figure 2. Input file for SAM7CA1CO2.

```

INCON---1---*---2---*---3---*---4---*---5---*---6---*---7---*---8
CO211
      1.000e5
      10.50
      0.
      20.
      0.00164
      0.e-4

MIX21
      1.000e5
      10.50
      0.
      20.
      0.000849
      0.e-4

AIR31
      1.000e5
      10.50
      0.
      20.
      0.0000
      0.e-4

CO212
      1.000e6
      10.50
      0.
      20.
      0.0164
      0.e-4

MIX22
      1.000e6
      10.50
      0.
      20.
      0.00852
      0.e-4

AIR32
      1.000e6
      10.50
      0.
      20.
      0.0000
      0.e-4

ELEME---1---*---2---*---3---*---4---*---5---*---6---*---7---*---8
CO211      10.1000E+010.1000E+01      0.5000E+000.5000E+00-.5000E+00
MIX21      10.1000E+010.0000E+00      0.5000E+000.5000E+00-.1500E+01
AIR31      10.1000E+010.1000E+01      0.5000E+000.5000E+00-.2500E+01
CO212      10.1000E+010.1000E+01      0.5000E+000.1500E+01-.5000E+00
MIX22      10.1000E+010.0000E+00      0.5000E+000.1500E+01-.1500E+01
AIR32      10.1000E+010.1000E+01      0.5000E+000.1500E+01-.2500E+01

CONNE

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

```

Figure 2. (continued). Input file for SAM7CA1CO2.

SAM7CA1CO2 ... Verification problem for EOS7CA.

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

THE TIME IS 0.115741E-13 DAYS

#####

TOTAL TIME	KCYC	ITER	ITERC	KON	DX1M	DX2M	DX3M	MAX. RES.	NER	KER	DELTEX
0.100000E-08	1	1	1	2	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	1	1	0.10000E-08

#####

NCG = CO2

ELEM.	INDEX	P (PA)	T (DEG-C)	SL	XBRINE (LIQ)	XNCG (LIQ)	XAIR (LIQ)	XAIR (GAS)	XNCG (GAS)	XTRC (GAS)	DG (KG/M**3)
CO211	1	0.10000E+06	0.20000E+02	0.50000E+00	0.00000E+00	0.16400E-02	0.52586E-07	0.21880E-02	0.98815E+00	0.00000E+00	0.17886E+01
MIX21	2	0.10000E+06	0.20000E+02	0.50000E+00	0.00000E+00	0.84900E-03	0.75991E-05	0.37756E+00	0.61085E+00	0.00000E+00	0.14921E+01
AIR31	3	0.10000E+06	0.20000E+02	0.50000E+00	0.00000E+00	0.00000E+00	0.15699E-04	0.98532E+00	0.00000E+00	0.00000E+00	0.11779E+01
CO212	4	0.10000E+07	0.20000E+02	0.50000E+00	0.00000E+00	0.16400E-01	0.25049E-05	0.10428E-01	0.98866E+00	0.00000E+00	0.19033E+02
MIX22	5	0.10000E+07	0.20000E+02	0.50000E+00	0.00000E+00	0.85200E-02	0.78353E-04	0.38796E+00	0.61091E+00	0.00000E+00	0.15359E+02
AIR32	6	0.10000E+07	0.20000E+02	0.50000E+00	0.00000E+00	0.00000E+00	0.16036E-03	0.99855E+00	0.00000E+00	0.00000E+00	0.11887E+02

#####

•
•
•

#####

^L

SAM7CA1CO2 ... Verification problem for EOS7CA.

KCYC = 1 - ITER = 1 - TIME =0.100000E-08

ELEM.	INDEX	P	T	SL	DX1	DX2	H (GAS) (J/KG)	pncg/px	K (GAS)	K (LIQ.)	VIS (GAS) (PA S)
CO211	1	0.10000E+06	0.20000E+02	0.50000E+00	0.00000E+00	0.00000E+00	0.51697E+06	0.97336E+00	0.41589E+00	0.21697E-06	0.14366E-04
MIX21	2	0.10000E+06	0.20000E+02	0.50000E+00	0.00000E+00	0.00000E+00	0.44386E+06	0.50366E+00	0.41589E+00	0.21697E-06	0.16973E-04
AIR31	3	0.10000E+06	0.20000E+02	0.50000E+00	0.00000E+00	0.00000E+00	0.32514E+06	0.00000E+00	0.41589E+00	0.21697E-06	0.20032E-04
CO212	4	0.10000E+07	0.20000E+02	0.50000E+00	0.00000E+00	0.00000E+00	0.48832E+06	0.98193E+00	0.41589E+00	0.21697E-06	0.14750E-04
MIX22	5	0.10000E+07	0.20000E+02	0.50000E+00	0.00000E+00	0.00000E+00	0.41540E+06	0.50775E+00	0.41589E+00	0.21697E-06	0.17379E-04
AIR32	6	0.10000E+07	0.20000E+02	0.50000E+00	0.00000E+00	0.00000E+00	0.29391E+06	0.00000E+00	0.41589E+00	0.21697E-06	0.20444E-04

#####

Figure 3. Portions of output file for SAM7CA1CO2 showing results at various conditions.

Table 5. Properties of CO₂-Air-H₂O mixtures at 1 bar and 20 °C.

	gas phase			
	x_g^{Air}	$x_g^{\text{CO}_2}$	ρ (kg m ⁻³)	μ (Pa s)
EOS7CA	3.26×10^{-3}	0.973	1.79	1.44×10^{-5}
Reference ^{1,2}	0.	1.	1.81	1.47×10^{-5}
EOS7CA	0.496	0.504	1.49	1.70×10^{-5}
Reference ³	0.5	0.5	1.50	1.65×10^{-5}
EOS7CA	0.977	0.	1.18	2.00×10^{-5}
Reference ^{1,2}	1.	0.	1.15	1.76×10^{-5}

¹NIST Chemistry WebBook thermophysical properties, 2013

²Air approximated as N₂ in NIST Chemistry WebBook

³Mixture approximated as 0.395-0.105-0.5 mole fraction N₂-O₂-CH₄ mixture in WebGasEOS.

Table 6. Properties of CO₂-Air-H₂O gas mixtures at 10 bars and 20 °C.

	gas phase			
	x_g^{Air}	$x_g^{\text{CO}_2}$	ρ (kg m ⁻³)	μ (Pa s)
EOS7CA	1.57×10^{-2}	0.982	19.03	1.47×10^{-5}
Reference ^{1,2}	0.	1.	19.10	1.48×10^{-5}
EOS7CA	0.490	0.510	15.36	1.74×10^{-5}
Reference ³	0.5	0.5	15.36	1.66×10^{-5}
EOS7CA	0.998	0.	11.89	2.04×10^{-5}
Reference ^{1,2}	1.	0.	11.52	1.77×10^{-5}

¹NIST Chemistry Webbook thermophysical properties webtool, 2013

²Air approximated as N₂ in NIST Chemistry WebBook

³Mixture approximated as 0.395-0.105-0.5 mole fraction N₂-O₂-CH₄ mixture in WebGasEOS.

Table 7. Properties of N₂-Air-H₂O mixtures at 1 bar and 20 °C.

	gas phase			
	x _g ^{Air}	x _g ^{N₂}	ρ (kg m ⁻³)	μ (Pa s)
EOS7CA	3.64 × 10 ⁻³	0.973	1.14	1.72 × 10 ⁻⁵
Reference ^{1,2}	0.	1.	1.15	1.76 × 10 ⁻⁵
EOS7CA	0.471	0.505	1.16	1.85 × 10 ⁻⁵
Reference ³	0.5	0.5	1.17	1.77 × 10 ⁻⁵
EOS7CA	0.977	0.	1.18	2.00 × 10 ⁻⁵
Reference ^{1,2}	1.	0.	1.15	1.76 × 10 ⁻⁵

¹NIST Chemistry Webbook thermophysical properties webtool, 2013

²Air approximated as N₂ in NIST Chemistry WebBook

³Mixture approximated as 0.395-0.105-0.5 mole fraction N₂-O₂-CH₄ mixture in WebGasEOS.

Table 8. Properties of N₂-Air-H₂O gas mixtures at 10 bars and 20 °C.

	gas phase			
	x _g ^{Air}	x _g ^{N₂}	ρ (kg m ⁻³)	μ (Pa s)
EOS7CA	1.93 × 10 ⁻²	0.978	11.54	1.76 × 10 ⁻⁵
Reference ^{1,2}	0.	1.	11.52	1.77 × 10 ⁻⁵
EOS7CA	0.490	0.510	11.71	1.88 × 10 ⁻⁵
Reference ³	0.5	0.5	11.73	1.78 × 10 ⁻⁵
EOS7CA	0.998	0.	11.89	2.04 × 10 ⁻⁵
Reference ^{1,2}	1.	0.	11.52	1.77 × 10 ⁻⁵

¹NIST Chemistry Webbook thermophysical properties webtool, 2013

²Air approximated as N₂ in NIST Chemistry WebBook

³Mixture approximated as 0.395-0.105-0.5 mole fraction N₂-O₂-CH₄ mixture in WebGasEOS.

Table 9. Properties of CH₄-Air-H₂O mixtures at 1 bar and 20 °C.

	gas phase			
	x _g ^{Air}	x _g ^{CH₄}	ρ (kg m ⁻³)	μ (Pa s)
EOS7CA	6.21 × 10 ⁻³	0.970	0.663	1.10 × 10 ⁻⁵
Reference ^{1,2}	0.	1.	0.659	1.10 × 10 ⁻⁵
EOS7CA	0.472	0.504	0.911	1.39 × 10 ⁻⁵
Reference ³	0.5	0.5	0.922	1.37 × 10 ⁻⁵
EOS7CA	0.977	0.	1.18	2.00 × 10 ⁻⁵
Reference ^{1,2}	1.	0.	1.15	1.76 × 10 ⁻⁵

¹NIST Chemistry Webbook thermophysical properties webtool, 2013

²Air approximated as N₂ in NIST Chemistry WebBook

³Mixture approximated as 0.395-0.105-0.5 mole fraction N₂-O₂-CH₄ mixture in WebGasEOS.

Table 10. Properties of CH₄-Air-H₂O gas mixtures at 10 bars and 20 °C.

	gas phase			
	x _g ^{Air}	x _g ^{CH₄}	ρ (kg m ⁻³)	μ (Pa s)
EOS7CA	9.45 × 10 ⁻³	0.988	6.77	1.11 × 10 ⁻⁵
Reference ^{1,2}	0.	1.	6.70	1.11 × 10 ⁻⁵
EOS7CA	0.490	0.508	9.26	1.41 × 10 ⁻⁵
Reference ³	0.5	0.5	9.32	1.37 × 10 ⁻⁵
EOS7CA	0.998	0.	11.89	2.04 × 10 ⁻⁵
Reference ^{1,2}	1.	0.	11.52	1.77 × 10 ⁻⁵

¹NIST Chemistry Webbook thermophysical properties webtool, 2013

²Air approximated as N₂ in NIST Chemistry WebBook

³Mixture approximated as 0.395-0.105-0.5 mole fraction N₂-O₂-CH₄ mixture in WebGasEOS.

Table 11. Enthalpy of CO₂ (J kg⁻¹) in gas mixture.

	1.0 bar 20 °C ²	10 bar 20 °C ³
EOS7CA	5.170×10^5	4.883×10^5
Reference ¹	5.016×10^5	4.925×10^5

¹NIST Standard Reference Database 69 – March 2003 Release: NIST Chemistry WebBook.

² $x_g^{\text{CO}_2} = 0.973$ in EOS7CA, $x_g^{\text{CO}_2} = 1.0$ in NIST reference case.

³ $x_g^{\text{CO}_2} = 0.982$ in EOS7CA, $x_g^{\text{CO}_2} = 1.0$ in NIST reference case.

Table 12. Enthalpy of N₂ (J kg⁻¹) in gas mixture.

	1.0 bar 20 °C ²	10 bar 20 °C ³
EOS7CA	3.392×10^5	3.058×10^5
Reference ¹	3.041×10^5	3.020×10^6

¹NIST Standard Reference Database 69 – March 2003 Release: NIST Chemistry WebBook.

² $x_g^{\text{N}_2} = 0.973$ in EOS7CA, $x_g^{\text{N}_2} = 1.0$ in NIST reference case.

³ $x_g^{\text{N}_2} = 0.978$ in EOS7CA, $x_g^{\text{N}_2} = 1.0$ in NIST reference case.

Table 13. Enthalpy of pure CH₄ (J kg⁻¹) in gas mixture.

	1.0 bar 20 °C ²	10 bar 20 °C ³
EOS7CA	9.408×10^5	8.886×10^5
Reference ¹	8.988×10^5	8.897×10^5

¹NIST Standard Reference Database 69 – March 2003 Release: NIST Chemistry WebBook.

² $x_g^{\text{CH}_4} = 0.970$ in EOS7CA, $x_g^{\text{CH}_4} = 1.0$ in NIST reference case.

³ $x_g^{\text{CH}_4} = 0.988$ in EOS7CA, $x_g^{\text{CH}_4} = 1.0$ in NIST reference case.

5.2 SAM7CA2: CO₂ Injection into a Shallow Vadose Zone

Introduction

This test problem is prototypical of the kinds of injection and migration problems that EOS7CA was designed to handle. The problem consists of a shallow vadose zone with a water table at a depth of approximately 3 m. We assume there is a horizontal injection well at a depth of approximately 2.4 m, and that the well is long enough that the flow domain can be approximated as a two-dimensional (2D) Cartesian slice transverse (perpendicular) to the well. This test problem is designed to model field experiments aimed at studying how CO₂ will flow and migrate within the shallow subsurface following its arrival from a deep leaking geologic carbon sequestration site through a leakage pathway such as an abandoned well, fault, or fracture zone (e.g., Oldenburg et al., 2010a). Table 1 provides properties of the system, and Figure 4 shows the input file. Figure 5 shows excerpts from the EOS7CA output file for this run.

Figure 6a shows the Cartesian 2D transverse model system discretization and water table location. The top boundary is held at a constant pressure of 1 bar (10^5 Pa), zero CO₂ concentration, and 15 °C temperature. The right-hand side boundary is held at constant conditions corresponding to the initial condition which has a gravity-capillary equilibrium above the water table and liquid saturation equal to 0.5 at the top of the domain. The bottom boundary of the system is held at constant (aqueous-phase) fully saturated conditions and $P = 1.194$ bar (i.e., hydrostatic below the initial water table). The left-hand side boundary is closed to flow representing a mirror symmetry plane.

Results and general description of CO₂ migration

Figure 6b-d shows model results for three times during simulation of CO₂ injection from the horizontal well with an injection rate of 2.43 kg d⁻¹. As shown in Figure 6, the CO₂ exits the well directly into the unsaturated zone and creates a CO₂-rich zone around the well. The CO₂ spreads in all directions by pressure-gradient driving forces. Note the CO₂ gas pushes the water table down as shown by the deflection of the light-blue contour lines, and by the high CO₂ concentration in the gas where formerly saturated aqueous phase conditions prevailed. The CO₂ exits out the ground surface (top of model domain) at some time between 0.5 and 1 day. By 5 days, the region of CO₂ flux out the ground surface extends to more than 3 m from the trace of the well. Note the high mass fractions of CO₂ in the gas phase (nearly pure CO₂) consistent with prior results of leakage and seepage modeling (Oldenburg and Unger, 2003), and high soil-gas concentration gradient near the ground surface.

Table 14. Properties of the homogeneous vadose zone.

	Soil
Temperature (T)	15 °C
Porosity (ϕ)	0.30
Permeability (k)	$1 \times 10^{-12} \text{ m}^2$
Capillary Pressure (P_c)	van Genuchten ^{1,2} $\lambda = 0.2, S_{lr} = 0.11, \alpha = 8.5 \times 10^{-4} \text{ Pa}^{-1}, P_{max} = 1 \times 10^{10} \text{ Pa}, S_{ls} = 1.$
Relative permeability (k_r)	van Genuchten ^{1,2} $S_{lr} = 0.10, S_{gr} = 0.01$
Molec. diffusivity coefficients (d_{β}^k)	Liquid: $10^{-10} \text{ m}^2 \text{ s}^{-1}$ Gas: $10^{-5} \text{ m}^2 \text{ s}^{-1}$ $\theta = 1.0, P_0 = 10^5 \text{ Pa}$
Tortuosity (τ_{θ})	1.0
Saturation-dependent tortuosity (τ_{β})	Equal to relative permeability

¹Pruess et al. (1999; 2011)

² λ is m in van Genuchten (1980).

```

ROCKS-----1-----2-----3-----4-----5-----6-----7-----8
vados 2 2400. 0.3 1.00E-12 1.00E-12 1.00E-12 1.73 935.8
1.00E-10
7 0.2 0.1 1. 0.01
7 0.2 0.11 8.5e-4 1.e10 1.
tpbnd 2 2400. 0.3 1.00E-12 1.00E-12 1.00E-12 1.73 1.e5
1.00E-10
7 0.2 0.1 1. 0.01
7 0.2 0.11 8.5e-4 1.e10 1.
btbnd 2 2400. 0.3 1.00E-12 1.00E-12 1.00E-12 1.73 1.e5
1.00E-10
7 0.2 0.1 1. 0.01
7 0.2 0.11 8.5e-4 1.e10 1.
sdbnd 2 2400. 0.3 1.00E-12 1.00E-12 1.00E-12 1.73 1.e5
1.00E-10
7 0.2 0.1 1. 0.01
7 0.2 0.11 8.5e-4 1.e10 1.
wt 2 2400. 0.3 1.00E-12 1.00E-12 1.00E-12 1.73 935.8
1.00E-10
5 1.
1 0. 0. 1.

PARAM 123456789012345678901234
8 3 100 10010000010002000040 03000 0.00e-05
4.3200E+05 1. 9.8066
1.e-5
1.000000E+05 0.000000E+00 0.000000E+00 0.000000E+00
1.050000E+01 1.500000E+01

TIMES-----1-----2-----3-----4-----5-----6-----7-----8
3 1
4.320e+04 8.640E+04 4.320e+05

MULTI-----1-----2-----3-----4-----5-----6-----7-----8
5 5 2 8

SELEC-----1-----2-----3-----4-----5-----6-----7-----8
6 1 1

0.0000E+000.0000E+000.0000E+000.0000E+000.0000E+000.0000E+00
0.0000E+000.0000E+000.0000E+000.0000E+00 0.0000E+00
0.3303E+060.2220E+030.0000E+000.0000E+00 0.1000E-07

DIFFU-----1-----2-----3-----4-----5-----6-----7-----8
1.000E-05 1.000E-10
1.000E-05 1.000E-10
1.000E-05 1.000E-10
1.000E-05 1.000E-10
1.000E-05 1.000E-10

FOFT -----1-----2-----3-----4-----5-----6-----7-----8
A12 1
AV1 1
COFT -----1-----2-----3-----4-----5-----6-----7-----8
A11 1A12 1

START-----1-----2-----3-----4-----5-----6-----7-----8

GENER-----1-----2-----3-----4-----5-----6-----7-----8
AQ1 1 COM3 2.8100E-051.2520E+04 Cp=835.0 J/kg/K

ENDCY
MESHMAKER1-----*-----2-----*-----3-----*-----4-----*-----5-----*-----6-----*-----7-----*-----8
XYZ
0.00
NX 1 1.
NY 1 .05
NY 49 .1
NZ 1 1.e-9
NZ 50 .1
NZ 1 2.e-9

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

```

Figure 4. Input file SAM7CA2 for CO₂ injection into shallow vadose zone.

```

AWX 1( 56, 7) ST = 0.398556E+06 DT = 0.542880E+05 DX1= 0.344122E+01 DX2= 0.000000E+00 T = 15.000 P = 100258. S = 0.401320E-03 ICURV=0
...ITERATING... AT [ 57, 1] --- DELTEX = 0.334440E+05 MAX. RES. = 0.794342E-01 AT ELEMENT AVO 1 EQUATION 3
...ITERATING... AT [ 57, 2] --- DELTEX = 0.334440E+05 MAX. RES. = 0.546936E-01 AT ELEMENT AWX 1 EQUATION 1
...ITERATING... AT [ 57, 3] --- DELTEX = 0.334440E+05 MAX. RES. = 0.488744E-02 AT ELEMENT AWX 1 EQUATION 1
...ITERATING... AT [ 57, 4] --- DELTEX = 0.334440E+05 MAX. RES. = 0.142935E-04 AT ELEMENT AWX 1 EQUATION 1
AWX 1( 57, 5) ST = 0.432000E+06 DT = 0.334440E+05 DX1= 0.439866E+01 DX2= 0.000000E+00 T = 15.000 P = 100263. S = 0.629840E-03 ICURV=0
^L
simple soil for shallow CO2 release by perforated pipe.

```

OUTPUT DATA AFTER (57, 5)-2-TIME STEPS THE TIME IS 0.500000E+01 DAYS

#####

TOTAL TIME	KCYC	ITER	ITERC	KON	DX1M	DX2M	DX3M	MAX. RES.	NER	KER	DELTEX
0.432000E+06	57	5	306	2	0.26870E+02	0.00000E+00	0.24887E-03	0.23839E-09	1696	1	0.33444E+05

#####

NGC = CO2

ELEM.	INDEX	P (PA)	T (DEG-C)	SL	XBRINE (LIQ)	XNCG (LIQ)	XAIR (LIQ)	XAIR (GAS)	XNCG (GAS)	XTRC (GAS)	DG (KG/M**3)
A11	1	0.10010E+06	0.15000E+02	0.50000E+00	0.00000E+00	0.20551E-62	0.15816E-04	0.98933E+00	0.15920E-59	0.00000E+00	0.12024E+01
A21	1	0.10013E+06	0.15000E+02	0.50187E+00	0.00000E+00	0.55279E-03	0.11310E-04	0.61716E+00	0.37355E+00	0.00000E+00	0.13804E+01
A31	1	0.10018E+06	0.15000E+02	0.50558E+00	0.00000E+00	0.11972E-02	0.60607E-05	0.28783E+00	0.70410E+00	0.00000E+00	0.15896E+01
A41	1	0.10023E+06	0.15000E+02	0.50930E+00	0.00000E+00	0.15542E-02	0.31547E-05	0.13976E+00	0.85272E+00	0.00000E+00	0.17066E+01
A51	1	0.10028E+06	0.15000E+02	0.51309E+00	0.00000E+00	0.17454E-02	0.16023E-05	0.68515E-01	0.92424E+00	0.00000E+00	0.17698E+01
A61	1	0.10032E+06	0.15000E+02	0.51700E+00	0.00000E+00	0.18452E-02	0.79471E-06	0.33369E-01	0.95952E+00	0.00000E+00	0.18032E+01
A71	1	0.10037E+06	0.15000E+02	0.52107E+00	0.00000E+00	0.18964E-02	0.38437E-06	0.15989E-01	0.97697E+00	0.00000E+00	0.18206E+01
A81	1	0.10042E+06	0.15000E+02	0.52533E+00	0.00000E+00	0.19224E-02	0.18085E-06	0.74862E-02	0.98550E+00	0.00000E+00	0.18297E+01
A91	1	0.10047E+06	0.15000E+02	0.52980E+00	0.00000E+00	0.19354E-02	0.82495E-07	0.34060E-02	0.98960E+00	0.00000E+00	0.18346E+01
AA1	1	0.10053E+06	0.15000E+02	0.53452E+00	0.00000E+00	0.19422E-02	0.36340E-07	0.14981E-02	0.99152E+00	0.00000E+00	0.18375E+01
AB1	1	0.10058E+06	0.15000E+02	0.53950E+00	0.00000E+00	0.19459E-02	0.15388E-07	0.63369E-03	0.99239E+00	0.00000E+00	0.18394E+01
AC1	1	0.10065E+06	0.15000E+02	0.54478E+00	0.00000E+00	0.19482E-02	0.62299E-08	0.25635E-03	0.99278E+00	0.00000E+00	0.18410E+01
AD1	1	0.10071E+06	0.15000E+02	0.55040E+00	0.00000E+00	0.19500E-02	0.23971E-08	0.98561E-04	0.99294E+00	0.00000E+00	0.18424E+01
AE1	1	0.10079E+06	0.15000E+02	0.55639E+00	0.00000E+00	0.19516E-02	0.87048E-09	0.35764E-04	0.99301E+00	0.00000E+00	0.18438E+01
AF1	1	0.10087E+06	0.15000E+02	0.56281E+00	0.00000E+00	0.19533E-02	0.29599E-09	0.12151E-04	0.99304E+00	0.00000E+00	0.18453E+01
AG1	1	0.10096E+06	0.15000E+02	0.56971E+00	0.00000E+00	0.19551E-02	0.93407E-10	0.38310E-05	0.99305E+00	0.00000E+00	0.18470E+01
AH1	1	0.10106E+06	0.15000E+02	0.57717E+00	0.00000E+00	0.19571E-02	0.27109E-10	0.11107E-05	0.99306E+00	0.00000E+00	0.18489E+01
AI1	1	0.10117E+06	0.15000E+02	0.58531E+00	0.00000E+00	0.19594E-02	0.71842E-11	0.29402E-06	0.99307E+00	0.00000E+00	0.18510E+01
AJ1	1	0.10131E+06	0.15000E+02	0.59425E+00	0.00000E+00	0.19620E-02	0.17442E-11	0.71288E-07	0.99308E+00	0.00000E+00	0.18535E+01
AK1	1	0.10147E+06	0.15000E+02	0.60418E+00	0.00000E+00	0.19651E-02	0.40276E-12	0.16435E-07	0.99309E+00	0.00000E+00	0.18565E+01
AL1	1	0.10166E+06	0.15000E+02	0.61524E+00	0.00000E+00	0.19689E-02	0.99191E-13	0.40398E-08	0.99311E+00	0.00000E+00	0.18601E+01
AM1	1	0.10191E+06	0.15000E+02	0.62731E+00	0.00000E+00	0.19738E-02	0.30522E-13	0.12401E-08	0.99312E+00	0.00000E+00	0.18647E+01
AN1	1	0.10223E+06	0.15000E+02	0.63963E+00	0.00000E+00	0.19802E-02	0.11710E-13	0.47425E-09	0.99314E+00	0.00000E+00	0.18707E+01
AO1	1	0.10268E+06	0.15000E+02	0.65033E+00	0.00000E+00	0.19891E-02	0.48231E-14	0.19446E-09	0.99318E+00	0.00000E+00	0.18791E+01
AP1	1	0.10338E+06	0.15000E+02	0.65557E+00	0.00000E+00	0.20028E-02	0.20180E-14	0.80807E-10	0.99322E+00	0.00000E+00	0.18921E+01
AQ1	1	0.10463E+06	0.15000E+02	0.64689E+00	0.00000E+00	0.20274E-02	0.10019E-14	0.39636E-10	0.99330E+00	0.00000E+00	0.19153E+01
AR1	1	0.10379E+06	0.15000E+02	0.68041E+00	0.00000E+00	0.20108E-02	0.94049E-13	0.37513E-08	0.99325E+00	0.00000E+00	0.18996E+01
AS1	1	0.10339E+06	0.15000E+02	0.70535E+00	0.00000E+00	0.20030E-02	0.24480E-11	0.98019E-07	0.99322E+00	0.00000E+00	0.18923E+01
AT1	1	0.10317E+06	0.15000E+02	0.72712E+00	0.00000E+00	0.19986E-02	0.31993E-10	0.12838E-05	0.99321E+00	0.00000E+00	0.18882E+01

Figure 5. Portion of output file for the shallow vadose zone problem SAM7CA2.

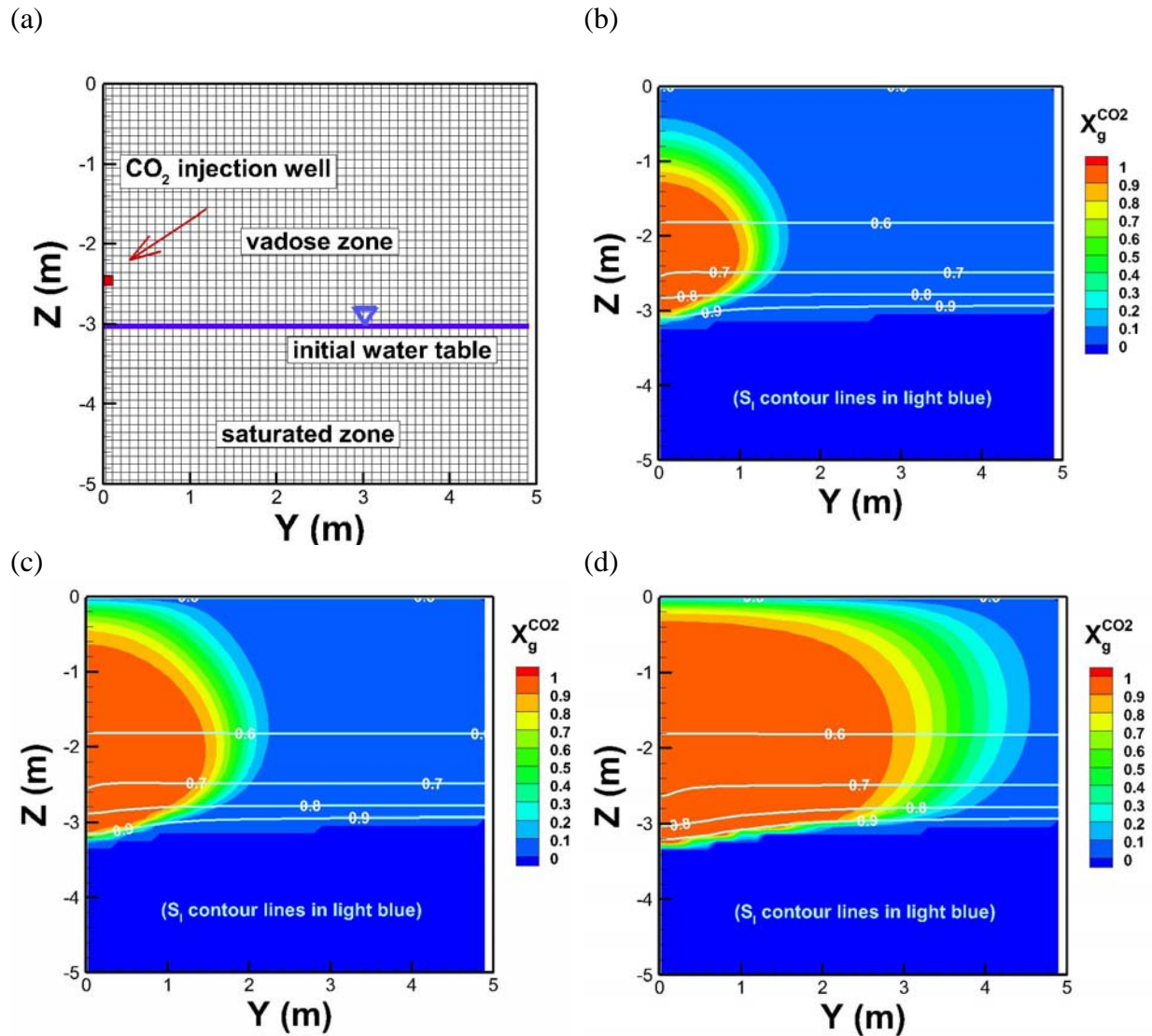


Figure 6. EOS7CA simulation results for the SAM7CA2 vadose zone problem showing discretization and locations of injection well and water table (a), and color contours of CO_2 mass fraction in the gas phase and light blue lines of aqueous phase saturation at (b) 0.5 days, (c) 1 day, and (d) 5 days.

6. Final Notes

Summary of important points to remember in using EOS7CA:

- Users should have access to the TOUGH2 User's Guide (Pruess et al., 2011) for supplementary general TOUGH2 information.
- NKIN controls the type of INCON file or block to be read from. For NKIN = NK, the INCON file is expected to be in the EOS7CA format with up to six primary variables. For NKIN = 2 or 3, the INCON is expected to be in standard EOS7 format with up to four primary variables.
- MOP(20) selects whether to reset variables to ensure that negative mass fractions do not occur (see p. 20 of this report for details).
- The SELEC parameters IE(14), IE(15), and IE(16) control the enthalpy calculation, the equation of state, and the choice of NCG, respectively.
- Although the gas mixture densities are very accurate in EOS7CA, no effects of dissolved gas components on liquid density are included.
- The intended application area of EOS7CA is shallow (e.g., vadose zone) flow of NCG (CO₂, N₂, or CH₄) with a gas tracer, air, and water vapor. The part of the gas phase that is not made up of NCG, tracer, and water vapor is assumed to be air.
- If molecular diffusivity is input as a negative number, the absolute value of this number is used for the phase molecular diffusivity without modification by S and τ (saturation and tortuosity) and without pressure or temperature effects.
- Pressure (P) affects gas diffusivity by the factor $1.0 \times 10^5/P$ (Pruess et al., 2011). For example, if pressure is 2.0×10^5 Pa, the effective molecular diffusivity for the

gas is one-half the input value.

- Temperature affects gas diffusivity by the factor $((T + 273.15)/273.15)^{\text{TEXP}}$ (Pruess et al., 1999; 2011). If TEXP is input as zero, temperature effects on gas diffusivity are neglected.

Acknowledgments

This work was carried out under the Zero Emissions Research and Technology project funded by the Assistant Secretary for Fossil Energy, Office of Coal and Power Systems through the National Energy Technology Laboratory, and by Lawrence Berkeley National Laboratory under Department of Energy Contract No. DE-AC02-05CH11231. We thank Stefan Finsterle and Christine Doughty (LBNL) for internal reviews.

Nomenclature

<i>d</i>	molecular diffusivity	$\text{m}^2 \text{ s}^{-1}$
<i>H</i>	enthalpy	J kg^{-1}
<i>Kh</i>	Henry's coefficient	Pa
<i>MW</i>	molecular weight	kg mole^{-1}
NCG	non-condensable gas	
NEQ	number of equations per grid block	
NK	number of mass components (species)	
NKIN	number of mass components (species) in INCON file or block	
NPH	maximum number of phases present	
<i>P</i>	pressure	Pa
<i>R</i>	gas constant ($8.31433 \text{ J kg}^{-1} \text{ }^\circ\text{C}^{-1}$)	$\text{J kg}^{-1} \text{ K}^{-1}$
<i>S</i>	phase saturation	-
<i>t</i>	time	sec.

T	temperature	°C, K
V	volume	m^3
\bar{V}_i	partial molar volume	$\text{m}^3 \text{mol}^{-1}$
x	mole fraction in the liquid phase	-
X	mass fraction	-
y	mole fraction in the gas phase	-
Y	Y-coordinate	m
Z	Z-coordinate	m
Z	Z factor (compressibility factor)	-

Greek symbols

μ	dynamic viscosity	$\text{kg m}^{-1} \text{s}^{-1}$
ϕ	porosity	-
ρ	density	kg m^{-3}
τ	tortuosity	-

Subscripts and superscripts

aq	aqueous phase
g	gas phase
ig	ideal gas
l, liq	liquid
0	reference value
β	phase
κ	mass components

References

- Battistelli, A., C. Calore, and K. Pruess (1997). The simulator TOUGH2/EWASG for modeling geothermal reservoirs with brines and non-condensable gas, *Geothermics*, 26(4), 437–464.
- Chung, T.-H., M. Ajlan, L.L. Lee, and K.E. Starling (1988). Generalized multiparameter correlation for nonpolar and polar fluid transport properties, *Ind. Eng. Chem. Res.*, 27, 671–679.
- Cramer, S.D. (1982). The solubility of methane, carbon dioxide and oxygen in brines from 0 to 300 °C , *U.S. Bureau of Mines Report No. 8706*.
- D'Amore, F., and A.H. Truesdell (1988). A review of solubilities and equilibrium constants for gaseous species of geothermal interest, *Sci. Geol. Bull.*, 41(3–4), 309–332, Strasbourg, France.
- Lewicki, J. L., G. E. Hilley, M. L. Fischer, L. Pan, C. M. Oldenburg, L. Dobeck, and L. Spangler (2009). Eddy covariance observations of surface leakage during shallow subsurface CO₂ releases, *J. Geophys. Res.*, 114, D12302. LBNL-1879E
- NIST Standard Reference Database 69 –NIST Chemistry Web Book, <http://webbook.nist.gov>, (retrieved during May 2013).
- Oldenburg, C.M., and A.J.A. Unger (2003). On leakage and seepage from geologic carbon sequestration sites: unsaturated zone attenuation, *Vadose Zone Journal*, 2(3), 287-296. LBNL-51928.
- Oldenburg, C.M., J.L. Lewicki, L. Dobeck, and L. Spangler (2010a). Modeling gas transport in the shallow subsurface during the ZERT CO₂ release test, *Transport in Porous Media*, 82(1), p. 77-92. LBNL-1529E.
- Oldenburg, C.M., J.L. Lewicki, L. Pan, L. Dobeck, and L. Spangler (2010b). Origin of the patchy emission pattern at the ZERT CO₂ release test, *Env. Earth Sci.*, 60(2), 241-250. LBNL- 3063E.
- Oldenburg, C.M., and K. Pruess (1995). EOS7R: Radionuclide transport for TOUGH2, Lawrence Berkeley Laboratory Report *LBL-34868*, Berkeley, California.

- Poling, B.E., J.M. Prausnitz, and J.P. O'Connell (2000). *The properties of gases and liquids, fifth edition*, McGraw Hill, New York.
- Prausnitz, J.M., R.N. Lichtenthaler, and E.G. de Azevedo (1986). *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, New York.
- Pruess, K., C.M. Oldenburg and G.J. Moridis (1999, 2012). TOUGH2 User's Guide Version 2. E. O. Lawrence Berkeley National Laboratory Report *LBNL-43134*, 1999; and *LBNL-43134 revised*).
- Reagan, M.T. (2006). WebGasEOS 1.0 User Guide, Lawrence Berkeley National Laboratory Report *LBNL/PUB-3188*.
- Reid, R.C., J.M. Prausnitz, and B.E. Poling (1987). *Properties of Gases and Liquids, Fourth Edition*, McGraw-Hill, 768 pp..
- Van Genuchten, M. Th. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal* 44.5, 892-898.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory is an equal opportunity employer.