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MODELING GAS RESERVOIR PROCESSES WITH TMVOC V.2.0

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ABSTRACT

TMVOC is a numerical reservoir simulator developed to model the three-phase non-isothermal flow of mixtures of water, non-condensible gases, volatile organic compounds (VOCs), and dissolved solids in multidimensional heterogeneous porous media. TMVOC was developed for application to shallow contamination problems that involve hydrocarbon fuel or organic solvent spills in the saturated and unsaturated zones. As such, TMVOC was formulated to model gas mixture properties and solubility at relatively low pressures appropriate to the vadose zone and shallow aquifers.

In TMVOC V.2.0, we have added new capabilities for modeling multicomponent mixtures over a range of pressures and temperatures from ambient to those found in natural gas reservoirs. In addition to the cubic equations of state for real gas mixtures already supported by the previous code version, TMVOC V.2.0 incorporates the Peng-Robinson (PR) EOS with binary interaction coefficients and the correlation to compute accurate viscosities for gas mixtures at high pressure. Thus, TMVOC is basically equivalent to the EOS7C module in the treatment of real gas mixture properties with the advantage that it can model a gas mixture with many more components. This capability will be useful for modeling carbon dioxide injection into gas reservoirs that contain a variety of gaseous species such as ethane, propane, and hydrogen sulfide.
As for the aqueous phase, one of the dissolved solids can be optionally defined as sodium chloride to model saline systems, using the same thermodynamic formulation developed for the EWASG module. In addition to CO_2 sequestration applications, TMVOC V.2.0 is a promising tool for applications dealing with the long term disposal of gases in underground reservoirs, such as the storage of acid gas mixtures produced in hydrocarbon fields all around the world.

The paper presents an overview of TMVOC V.2.0 and verification of gas mixture property estimates. We also present an application dealing with multiple gas species to demonstrate the code capabilities in modeling flow problems which involve complex gas mixtures.

THE TMVOC RESERVOIR SIMULATOR

TMVOC V.1.0 (Pruess and Battistelli, 2002; 2003) is a numerical simulator for three-phase non-isothermal flow of water, a user-defined set of gaseous species, and a mixture of VOCs in 3D heterogeneous porous media. An extension of the TOUGH2 general-purpose simulation program (Pruess et al., 1999), TMVOC was originally designed for applications to contamination problems that involve hydrocarbon fuel or organic solvent spills in the saturated and unsaturated zones. TMVOC V.1.0 has been available to the public since May 2002.

The mass components tracked by TMVOC V.1.0 are: water, a set of user-defined gases (which can be chosen among O_2, N_2, CO_2, CH_4, ethane, ethylene, acetylene, and pseudo-component air) and a set of user-defined VOCs (hydrocarbons or organic solvents). Gases available in the internal code data bank are either inorganic gases as well as organic gases having a critical temperature lower than ambient or in the range of temperatures found in conventional environmental applications. It is assumed that these mass components are distributed under thermodynamic equilibrium conditions in any of the three possible flowing phases: gas, aqueous, and NAPL. Any combination of the three phases and related possible phase transitions are modeled by TMVOC as shown in Fig. 1. The gas phase density and departure enthalpy can be computed using cubic equation-of-state (EOS) for real gas mixtures such as the Soave-Redlich-Kwong (SRK; Soave, 1972) and the PR (Peng and Robinson, 1976). Because of the low-pressure characteristic of environmental applications, binary interaction coefficients were assumed to be negligible. A detailed description of the thermodynamic and numerical formulations of TMVOC V.1.0, is given by Pruess and Battistelli (2002).

The simulator was further improved for the modeling of biodegradation reactions of organic compounds in the subsurface (Battistelli, 2003). An additional class of compounds, the dissolved solids, was also added. It is assumed that they do not partition in the gas and NAPL phases, but can optionally be adsorbed on the rock matrix and can decay according to a first order kinetic rate law. H_2S and NH_3 were added to the gases included in the internal data bank of the code.

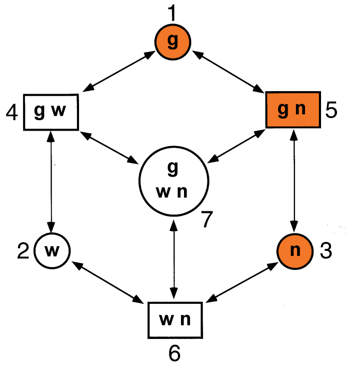

Figure 1. Phase combinations and phase transitions modeled by TMVOC. w, g and n stand for aqueous, gas and NAPL. Shaded phase combinations cannot be modeled when dissolved solids are treated.

TMVOC Version 2.0

For the modeling of coastal contaminated sites, where even shallow aquifers are often affected by sea water intrusion, the TMVOC simulator was further improved (V.2.0) to include capabilities for calculating the thermodynamic and transport properties of sodium chloride brines (Aquater, 2003). Correlations for calculating the brine vapor pressure, density, viscosity and enthalpy as a function of NaCl concentration, as well as the effects of salinity on the solubility of CO_2, CH_4, O_2, N_2, and air were taken from the EWASG module of the TOUGH2 simulator (Battistelli et al., 1997). The same treatment of brine properties was also implemented in the ECO2 EOS module developed to model the CO_2 sequestration in saline aquifers by Pruess and Garcia (2002).

Propane, n- and i-butane were included to the data bank of gases modeled by TMVOC V.2.0, with salting-out effects in the aqueous phase evaluated according to the approach suggested by Soreide and Whitson (1992). The possible precipitation of dissolved solids is not modeled by TMVOC, as it is in EWASG for the precipitation of halite. Thus, the code cannot simulate the disappearance of the aqueous phase when dissolved solids are included: these phase combinations are shaded in Fig.1. On the other hand, single-gas phase conditions can be specified for inactive elements to simulate atmospheric boundary conditions often needed for environmental applications.

MODELING HIGH PRESSURE GAS MIXTURES

The accurate evaluation of thermodynamic and transport properties of complex gas mixtures is of great interest in several fields of reservoir engineering, including the exploitation of natural gas fields, and the injection of CO_2 into depleted natural gas reservoirs for carbon sequestration with enhanced gas recovery (CSEGR) (Oldenburg et al., 2001).

The EOS7C module was developed for the TOUGH2 reservoir simulator to model non-isothermal multiphase and multi-component flow and transport in gas reservoirs (Oldenburg et al., 2001). EOS7C considers five mass components (water, brine, CO_2, gas tracer, CH_4) and heat. It incorporates a modified version of the PR EOS for calculating real gas mixture properties (density and enthalpy departures) across the entire range of relevant pressures and temperatures (Oldenburg and Benson, 2002). Modifications to the original PR EOS (Peng and Robinson, 1976) were developed by Soreide and Whitson (1992) to accurately model the thermodynamic properties of mixtures of light hydrocarbons (CH_4, ethane, propane, n-butane) and inorganic gases (CO_2, H_2S, N_2) commonly associated with hydrocarbon reservoirs, in equilibrium with high salinity sodium chloride brines. These modifications were aimed to:

- accurately reproduce the brine vapor pressure as function of temperature and salinity;
- evaluate reliable binary interaction coefficients between mixture pairs accounting for temperature and salinity effects.

Gas mixture viscosity is calculated within EOS7C following the model of Chung et al. (1988), whereas the solubility of CO_2 and CH_4 is evaluated including the effects of temperature and salinity following the salting-out approach and the experimental results of Cramer (1982), but still neglecting fugacity effects. Verification of physical property calculations in the system CH_4-CO_2-H_2O was done by comparing EOS7C results against published data and models at pressures and temperatures relevant for CSEGR applications (Oldenburg and Benson, 2002).

The modified PR EOS for real gas mixtures presently included in EOS7C is in principle able to handle a set of chemical compounds including CH_4, ethane, propane, H_2S, CO_2, N_2, and H_2O, which are the normal constituents of natural gas reservoirs and are also involved in CSEGR operations. The modified PR EOS was then included into TMVOC V.2.0, as an alternative to the original cubic EOS supported, to allow the evaluation of density, departure enthalpy and dynamic viscosity of multi-component gas mixtures at high pressure and in equilibrium with sodium chloride brines. For its numerical formulation, TMVOC V.2.0 has in principle no limits about the number of gaseous compounds to be modeled. However, this number is limited for practical purposes to 10 in the present version. Thus, TMVOC is basically equivalent to the EOS7C module in the treatment of real gas mixture properties with the advantage that it can model a gas mixture with more components. This capability is useful for the modeling of CO_2 injection into natural gas reservoirs that contain a variety of gaseous species such as ethane, propane, H_2S and N_2. These components are in fact found in typical natural gas reservoirs as shown in Table 1 (McCain, 1990).

Table 1. Composition of typical natural gas (McCain, 1990).

Component	Molar fraction
Methane	70 – 98 %
Ethane	1 – 10 %
Propane	trace – 5%
Butanes	trace – 2%
Pentanes	trace – 1%
Hexanes	trace – 0.5%
Heptanes +	trace – 0.5%
Nitrogen	trace – 15%
Carbon dioxide *****	trace – 5%
Hydrogen sulfide *****	trace – 3%
Helium	none – 5%

***** *Occasionally natural gases are found which are predominately carbon dioxide or hydrogen sulfide.*

In addition to CO_2 sequestration applications, TMVOC V.2.0 is a promising tool for the numerical modeling of the long term storage of other gas mixtures in underground reservoirs, such as the disposal of acid gases obtained during the sweetening process of sour natural gases produced in many hydrocarbon fields all around the world.

PRELIMINARY CODE VERIFICATION

Preliminary verification tests where performed comparing TMVOC V.2.0 against TOUGH2-EOS7C and other numerical codes (GEM (Computer Modelling Group Ltd., Canada) and SIMUSCOPP (Inst. Français du Pétrol, France)). Test problems were taken from a recent code inter-comparison study that is part of the US GeoSeq project (Oldenburg et al., 2002).

Comparison of Physical Property Estimates

The first comparison we present is for density (ρ), viscosity (μ), and solubility (X_L) of CO_2 and CH_4 gas mixtures. As the critical pressure and temperature of CO_2 (73.8 bars, 31.0°C) will be reached in the subsurface at depths greater than approximately 800 m, injected CO_2 will most commonly be supercritical in the subsurface. Therefore, we present estimates of physical properties, for the end members and 50-50 mixtures, at both subcritical (Table 2: 40 bars) and supercritical (Table 3: 100 bars) conditions, computed using TMVOC and EOS7C. As shown in Tables 3 and 4, the gas mixture properties evaluated by TMVOC V.2.0 are substantially in agreement with those computed by EOS7C.

Table 2. Properties of CO_2 - CH_4 gas mixtures and aqueous solubility at 40° C and 40 bar.

	gas phase				aqueous phase	
Simulation code	X_G CH4	X_G CO2	ρ (kg/m^3)	μ (Pa s)	X_L CH4	X_L CO2
TMVOC V.2.0	0	9.98E-01	85.31	1.70E-05	0	1.62E-02
TOUGH2/EOS7C	0	1	85.45	1.70E-05	0	1.62E-02
Reference values	0	1	83.79	1.73E-05	0	1.37E-02
TMVOC V.2.0	4.99E-01	4.99E-01	51.94	1.44E-05	3.71E-04	8.11E-03
TOUGH2/EOS7C	0.5	0.5	51.97	1.44E-05	3.73E-04	8.07E-03
Reference values	0.5	0.5	51.33	1.67E-05	3.66E-04	6.74E-03
TMVOC V.2.0	9.98E-01	0	26.48	1.21E-05	7.42E-04	0
TOUGH2/EOS7C	1	0	26.42	1.21E-05	7.43E-04	0
Reference values	1	0	26.10	1.23E-05	7.22E-04	0

Table 3. Properties of CO_2 - CH_4 gas mixtures and aqueous solubility at 40° C and 100 bar.

	gas phase				aqueous phase	
Simulation code	X_G CH4	X_G CO2	ρ (kg/m^3)	μ (Pa s)	X_L CH4	X_L CO2
TMVOC V.2.0	0	9.98E-01	564.73	4.34E-05	0	4.06E-02
TOUGH2/EOS7C	0	1	566.00	4.35E-05	0	4.03E-02
Reference values	0	1	631.90	5.04E-05	0	2.19E-02
TMVOC V.2.0	4.99E-01	4.99E-01	155.23	1.81E-05	9.27E-04	2.03E-02
TOUGH2/EOS7C	0.5	0.5	155.16	1.81E-05	9.43E-04	2.00E-02
Reference values	0.5	0.5	153.97	1.94E-05	7.95E-04	1.21E-02
TMVOC V.2.0	9.98E-01	0	71.71	1.42E-05	1.86E-03	0
TOUGH2/EOS7C	1	0	71.57	1.41E-05	1.86E-03	0
Reference values	1	0	70.03	1.41E-05	1.54E-03	0

Reference values for gas phase density and dynamic viscosity in Tables 2 and 3 were computed using the NIST (1992) computer code. Reference values for CH_4 and CO_2 solubility in the aqueous phase are taken from Wagman et al. (1982), Spycher and Reed (1988), Shock et al. (1989), Johnson et al. (1992).

Mixing of Stably Stratified Gases (Problem #1)

In this problem, CO_2 and CH_4 gases are placed in contact one on top of the other, with the lighter CH_4 on top, in a 100 m long vertical column in the presence of an immobile aqueous phase. Gases mix as controlled by molecular diffusion and associated flow at 40 bar and 40°C under isothermal conditions. The domain, properties, boundary and initial conditions are described in detail by Oldenburg et al. (2002). Although the problem is dominated by diffusion, small advective fluxes arise as diffusive mixing around the interface leads to density changes that affect gas pressure. Figs. 2 and 3 present the pressure and CO_2 molar concentration profiles computed after 10 and 100 years of mixing by TMVOC (T), TOUGH2-EOS7C (E), GEM (G), and SIMUSCOPP (S).

The mole fraction profiles computed by TMVOC compare well with those of GEM and SIMUSCOPP, whereas the lower mole fractions computed at the bottom of the vertical column by EOS7C are mainly due to the slightly different initial conditions assumed. The differences shown in Fig. 2 for the pressure profile after 100 years of molecular diffusion are likely due to the differences among the codes in formulating the molecular diffusion flux.

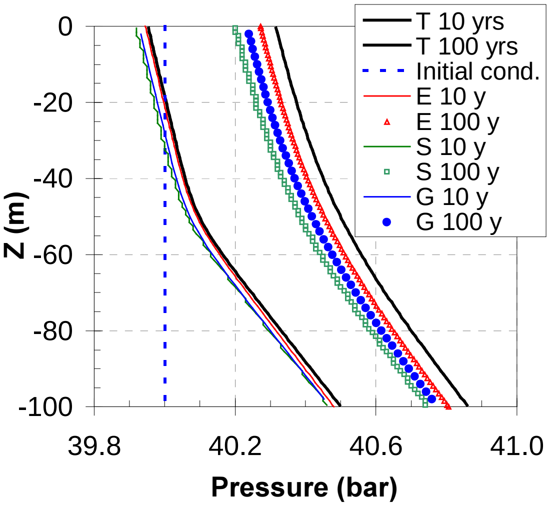

Figure 2. Simulated pressure profile as function of Z for Problem 1 at 0, 10 and 100 years (T=TMVOC, E=EOS7C, S=SIMUSCOPP, G=GEM).

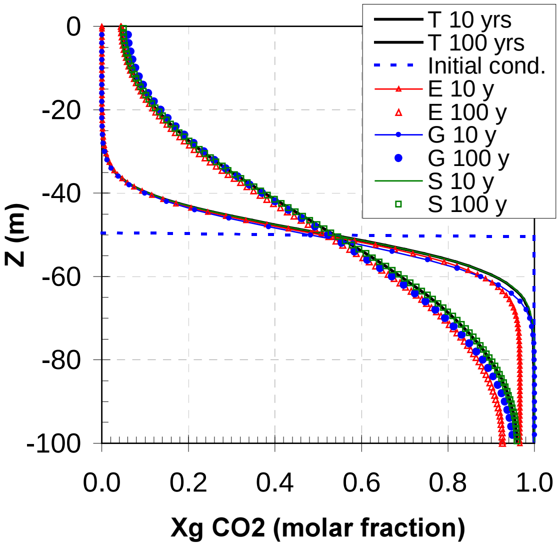

Figure 3. Simulated profile of CO_2 molar fraction in the gas phase as function of Z for Problem 1 at 0, 10 and 100 years (T=TMVOC, E=EOS7C, S=SIMUSCOPP, G=GEM).

Advective-Diffusive Mixing due to Lateral Density Gradient (Problem #2)

In this problem CO_2 and CH_4 gases are placed side-by-side (with CO_2 on the left) in a 2D vertical slice with dimensions of 100 m by 100 m, and allowed to mix for 100 years. Complete problem specifications are given by Oldenburg et al., (2002). The strong lateral density gradient between the dense CO_2 gas and the relatively light CH_4 gas causes a strong density-driven flow where CO_2 tends to move downward and CH_4 tends to move upward to the top of the reservoir. Comparison of results is presented in Fig. 4 as horizontal profiles of CO_2 mole fraction in the gas phase at Z=–50 m and at two different times of 0.5 and 5 years.

As shown in Fig. 4, variations in results between the four codes are more pronounced than for the previous Test Problem. Thus, larger differences can be expected for cases of more complex flow and transport, even though some of the differences can be linked to slightly different problem formulations used with the different codes.

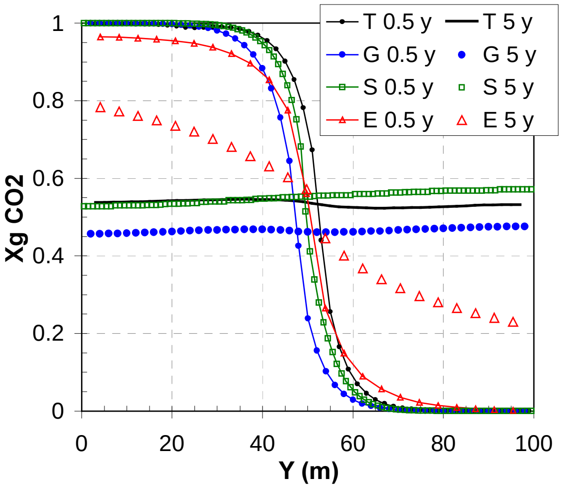

Figure 4. Simulated horizontal profile of CO_2 molar fraction in the gas phase at Z=–50 m for Test Problem 2 at 0.5 and 5 years (T=TMVOC, E=EOS7C, S=SIMUSCOPP, G=GEM).

CODE DEMONSTRATION

The capability of TMVOC to simulate the relevant processes occurring in CSEGR applications are here tested by modeling CO_2 injection in a depleted natural gas reservoir.

The problem is patterned after the EOS7C application to the Rio Vista gas field, located in California, presented by Oldenburg et al. (2001), even though no attempts to replicate the EOS7C results are made here. Two versions of the problem are discussed: *A*) injection of pure CO_2 in the reservoir containing pure CH_4; *B*) injection of a CO_2-N_2 mixture (80% – 20% by mass) into the gas reservoir containing a CH_4-ethane mixture (92% – 8% by mole fraction).

The modeling study is performed using a 2-D model based on the simplified representation of Rio Vista field used by Oldenburg et al. (2001). We use a 1 km wide cross-section with vertical dimension 100 m and horizontal extent 6600 m. The model system was discretized into 660 grid blocks (33 x 20) of sizes 200 m x 5 m in Y and Z-directions, respectively, with roof sloping at 0.78 degrees to the west, here corresponding to the left of our model. We assume the reservoir is already depleted by previous gas production, with initial conditions corresponding to a pressure of 40 bar at the water table located at Z=0 on the left side of the simulation domain. Initial conditions within the reservoir were determined by running the system to steady state under the effects of gravity and capillary forces. Pure water properties are also assumed for the aqueous phase. Model properties are summarized in Table 4.

Table 4. Relevant properties of simplified reservoir model used for code demonstration (after Oldenburg et al., 2001).

Property	**Value, units**
Porosity	0.35
Horizontal permeability	1.0×10^{-12} m^2
Vertical permeability	1.0×10^{-14} m^2
Capillary pressure	Van Genuchten (1980)
m, S_{lr}, $1/P_o$	0.2, 0.27, 8.4×10^{-4} Pa^{-1}
P_{max}, S_{ls}	-10^{+5} Pa, 1
Relative permeability	
- liquid phase	Van Genuchten model
- gas phase	Corey model, S_{gr}=0.01
Molecular diffusivity gas	1.0×10^{-5} m^2 s^{-1}
Molecular diffusivity liq.	1.0×10^{-10} m^2 s^{-1}
temperature	65°C
Initial pressure at water table	40 bar abs
Case *A*: reservoir gas	100% CH_4
Case *B*: reservoir gas	92% CH_4, 8% ethane
Gas injection rate	8.2 kg/s
Constant extraction press.	39 bar abs

We simulate 20 years of CSEGR operation, with gas injection taking place at a rate of 8.2 kg/s at a depth of 15 m below reservoir roof and at Y=1900 m, whereas reservoir gas is produced from the upper right-side grid block through a well on deliverability. The CSEGR simulations are performed neglecting water drive effects, by assuming closed system boundaries. The simulated distribution of CO_2 mole fraction in the gas phase for case *A* (pure CO_2 injection) is shown in Fig. 5, where incipient mixing between injected CO_2 and reservoir gas is apparent at the well location after 10 years of CSEGR.

The gas production rate and the CO_2 mole fraction in the extracted fluid are shown in Fig. 6. After an initial increase, the total gas production rate becomes almost constant at a value of 1.95 kg/s from about 4 to 13 years, to increase afterwards when CH_4 mole fraction at the production well declines due to CO_2 breakthrough.

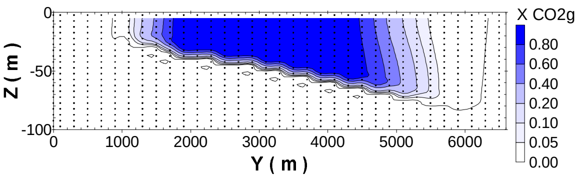

Figure 5. Case A: distribution of CO_2 molar fraction in the gas phase after 10 years of CO_2 injection and reservoir gas production.

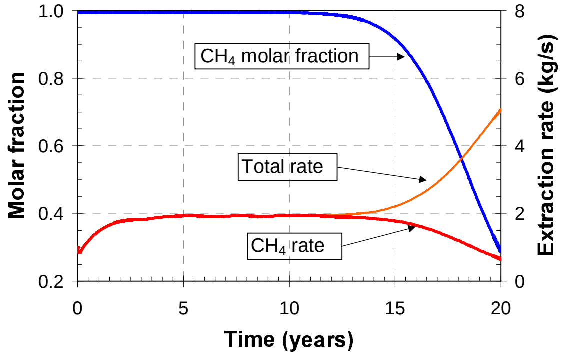

Figure 6. Case A: gas extraction rates and CH_4 mole fraction in extracted gas as function of time during CSEGR.

The simulated distribution of CO_2 mole fraction in the gas phase for case *B* (injection of the $CO_2 - N_2$ mixture) is shown in Fig. 7, where the breakthrough of CO_2 is apparent at the well location after 10 years of CSEGR. The breakthrough of injected gas is better shown in Fig. 8 where the molar composition of extracted reservoir gas is plotted as a function of time. The original reservoir gas composition starts to change after approx. 8 years, compared to the 11 years of case *A*.

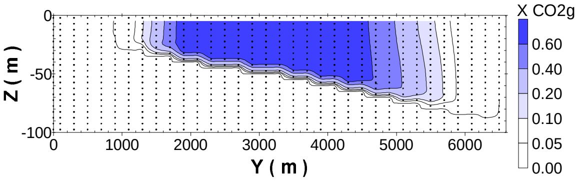

Figure 7. Case B: distribution of CO_2 molar fraction in the gas phase after 10 years of CO_2 - N_2 injection and reservoir gas production.

This faster breakthrough of injected gases can be explained from the density contrast between injected and reservoir gas for cases *A* and *B*. Density and dynamic viscosity of pure CH_4, pure CO_2 (case *A*) and of CH_4-ethane and CO_2-N_2 mixtures (Case *B*) are shown in Table 5. The density of original reservoir gas is 32.6% and 42.0% of the injected gas density, for Cases *A* and *B*, respectively, facilitating the mixing between injected and reservoir gas in Case *B*.

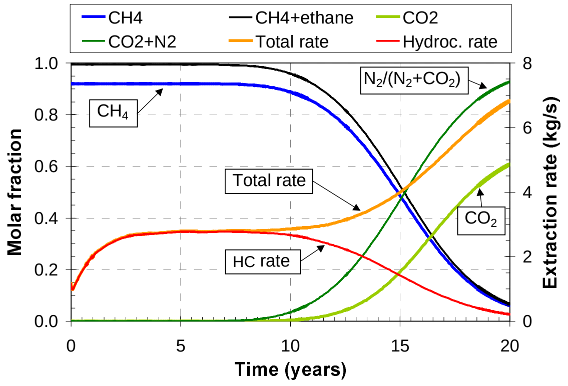

Figure 8. Case B: gas extraction rates and molar fractions of extracted gases as function of time during CSEGR.

Table 5. Density and viscosity of vapor saturated gas mixtures used for cases A and B at initial reservoir conditions (65° C and 40 bar).

Gas mixture	ρ (kg/m^3)	μ (Pa s)
CH_4	24.089	0.12804×10^{-4}
CO_2	73.861	0.17834×10^{-4}
92% CH_4 + ethane	26.030	0.12650×10^{-4}
71.9% CO_2 + N_2	61.954	0.18537×10^{-4}

The CO_2-N_2 gas mixture has a lower density than pure CO_2 at reservoir conditions. Thus, at constant injected mass rate, Case *B* injected gas mixture occupies a greater volume in the reservoir with a more efficient displacement of native gases.

The gas production rate from 5 to 10 years stabilizes to a value of approx. 2.75 kg/s against the 1.95 kg/s of Case *A*. It is also interesting to note that N_2 concentration at the well block is higher than in the injected fluid as shown in Fig. 9, where the ratio of N_2 molar fraction to (N_2+CO_2) molar fractions at the well block is always higher than the N_2 concentration in the injected mixture (28.1%), whereas the ethane/(ethane+CH_4) ratio remains always constant.

The mechanism responsible for N_2 enrichment at the well block with respect to the composition of injected gas mixture is the much lower solubility of N_2 in reservoir water than CO_2. Fig. 10 shows the N_2, O_2, CH_4 and CO_2 Henry's constant functions included in EWASG and implemented in TMVOC V.2.0. CO_2 aqueous solubility at 65°C is about 30 times higher than N_2 solubility. Thus, CO_2 dissolves preferentially in the aqueous phase and the CO_2 front is then retarded with respect to that of N_2. It must be pointed out that the aqueous solubility of gases at these reservoir conditions is overestimated by the present TMVOC version, and further studies of this effect using a more accurate solubility model are needed to understand better its significance.

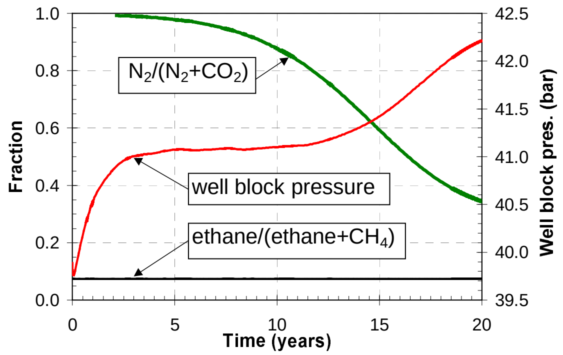

Figure 9. Case B: molar fractions of ethane and N_2 with respect to (ethane+CH_4) and (N_2+CO_2), respectively, at well block as function of time during CSEGR..

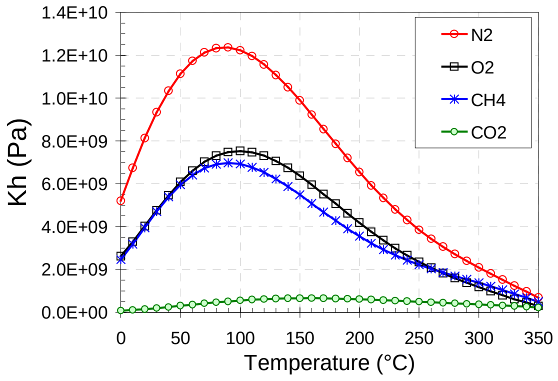

Figure 10. Henry's constant (Kh) values of N_2, O_2, CH_4 and CO_2 as function of temperature implemented in TMVOC V.2.0.

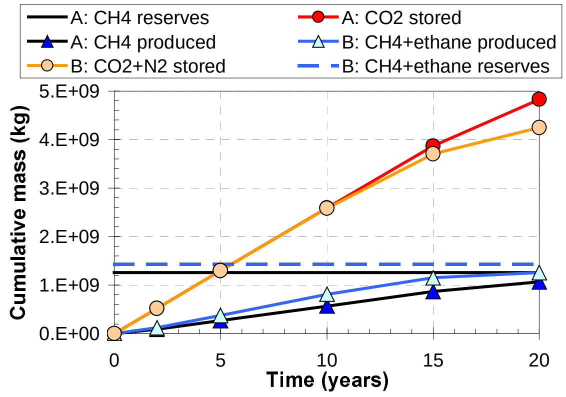

Figure 11. Initial hydrocarbon reserves, cumulative produced hydrocarbons, and stored injected gases during CSEGR, for Cases A and B.

Hydrocarbons produced and injected gas stored in the reservoir are shown in Fig 11 as function of time for

Case *A* and *B*, respectively. Initial hydrocarbon inventory is slightly higher for Case *B* due to the higher mixture molecular weight. The constant mass rate of injected gas produces a faster displacement of hydrocarbons for Case *B*, due to the higher specific volume of injected gas at reservoir conditions. Fig. 11 shows also the effects of the earlier breakthrough of injected gases on the efficiency of their disposal.

CONCLUSIONS

The TMVOC V.2.0 numerical simulator was coupled with a modified version of the PR EOS to model complex gas mixtures at high pressures. The PR EOS includes the modifications suggested by Soreide and Whitson (2002) to accurately model the phase behavior and mutual solubility of mixtures of light hydrocarbons (methane, ethane, and propane) and inorganic gases usually found in natural gas reservoirs (CO_2, H_2S and N_2) in equilibrium with high salinity brines. Gas mixture viscosity at high pressures is calculated as in EOS7C following the model of Chung et al. (1988). The solubility of gases is presently evaluated following a conventional Henry's law formulation, including the effects of temperature and salinity using the salting-out approach; thus, fugacity effects and Poynting correction which are import at high pressures are presently neglected.

Preliminary verification tests have been performed by comparing TMVOC V2.0 against TOUGH2-EOS7C and two other numerical simulators, GEM and SIMUSCOPP, by reproducing two sample problems formulated for an international code intercomparison study (Oldenburg et al., 2002). TMVOC V.2.0 results compare well with those of the other simulators. Some differences are noted which might be due both to different thermodynamic and numerical formulations, and to slight differences in problem specifications.

A code application to the modeling of CO_2 sequestration with enhanced gas recovery was discussed for code demonstration purposes. We presented the modeling of CSEGR in a sloping depleted natural gas reservoir using a numerical model patterned after the application of TOUGH2-EOS7C to the Rio Vista gas field (CA) performed by Oldenburg et al. (2001). We simulated two different cases for a total of 20 years each: *A*) injection of pure CO_2, with pure CH_4 in the reservoir; *B*) injection, at the same mass rate, of a mixture of CO_2 and N_2 (80% and 20% by mass, respectively) with a mixture of CH_4 and ethane in the reservoir (92% and 8% by molar fraction, respectively).

The lower density at reservoir conditions of gases injected for Case *B* led to a more efficient displacement of hydrocarbons in the reservoir, with higher extraction rates and early breakthrough of injected gases at the extraction well. The higher viscosity contrast between injected and reservoir gases for Case *B* helped also in a more efficient displacement of hydrocarbons. The higher solubility of CO_2 in the aqueous phase with respect to N_2 was responsible for a retardation of CO_2 in the injected gas front, so that the N_2/CO_2 ratio at the extraction well was always higher than at the injection well. The application shows that compositional effects can be important in modifying the transport properties of gas mixtures Thus, the compositional modeling of CSEGR operations might be justified when complex gas mixtures are involved. In such cases TMVOC V.2.0 can be the modeling tool of choice. We also point out that TMVOC allows also to define more than one gas component to be CO_2, or any other gas supported by the code. This means, for instance, that in a simulation we can distinguish the injected CO_2 from the CO_2 originally contained in the reservoir gas as a natural constituent.

TMVOC V.2.0 needs additional improvements to enhance the description of processes taking place during CO_2 sequestration in natural gas reservoirs. The modified PR EOS used should be improved by including n-butane among the gases already supported, following Soreide and Whitson (1992). Fugacity effects on the gas solubility in the aqueous phase should be taken into account as they are significant at the high pressures found in natural gas reservoirs and at conditions expected for CO_2 disposal. Even if solubility trapping ony makes a minor contribution to CO_2 sequestration in depleted natural gas reservoirs, the evaluation of gas solubility at high pressure is important for the reliable simulation of mixing processes between injected and original reservoir gases, as well as for the evaluation of fluid-rock interactions and related effects on rock properties.

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