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ECO2N - A NEW TOUGH2 FLUID PROPERTY MODULE FOR STUDIES OF CO$_2$ STORAGE IN SALINE AQUIFERS

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ABSTRACT

ECO2N is a fluid property module for the TOUGH2 simulator (Version 2.0) that was designed for applications to geologic storage of CO$_2$ in saline aquifers. It includes a comprehensive description of the thermodynamics and thermophysical properties of H$_2$O - NaCl - CO$_2$ mixtures, that reproduces fluid properties largely within experimental error for the temperature, pressure and salinity conditions of interest (10 ˚C ≤ T ≤ 110 ˚C; P ≤ 600 bar; salinity up to full halite saturation). Flow processes can be modeled isothermally or non-isothermally, and phase conditions represented may include a single (aqueous or CO$_2$-rich) phase, as well as two-phase mixtures. Fluid phases may appear or disappear in the course of a simulation, and solid salt may precipitate or dissolve. ECO2N can model super- as well as sub-critical conditions, but it does not make a distinction between liquid and gaseous CO$_2$. This paper highlights significant features of ECO2N, and presents illustrative applications.

INTRODUCTION

Numerical modeling is an important tool for studying the injection of CO$_2$ into saline aquifers, which is being considered as a means for reducing atmospheric emissions of this greenhouse gas. Simulating CO$_2$ storage in saline aquifers requires an accurate representation of the thermodynamics and thermophysical properties of brine-CO$_2$ mixtures. Our development of simulation capabilities for CO$_2$/aquifer systems started from the EWASG fluid property module (Battistelli et al., 1997). EWASG was designed for applications to geothermal reservoir engineering, which generally involve elevated temperatures and modest CO$_2$ partial pressures, typically of order 10 bar or less. In contrast, the thermodynamic regime of interest for CO$_2$ storage in saline formations typically involves moderate (near ambient) temperatures, and high CO$_2$ pressures of the order of a few hundred bars. Lower CO$_2$ pressures are of interest in connection with studies of CO$_2$ leakage from the primary storage reservoir.

Compared to the PVT formulation used in EWASG, the main enhancements required for CO$_2$ storage studies include (1) accurate correlations for density, viscosity, and specific enthalpy of CO$_2$ for temperatures from ambient to about 100 ˚C, and pressures from ambient to several hundred bar; (2) accurate representation of thermophysical properties of brines for the same temperature and pressure range, and (3) accurate partitioning of H$_2$O and CO$_2$ between aqueous and CO$_2$-rich phases.

CO$_2$ storage in saline aquifers would be made at supercritical conditions. However, if CO$_2$ leaks from the primary storage reservoir its temperature and pressure could drop below the critical point (T$_{crit}$ = 31.04 ˚C, P$_{crit}$ = 73.82 bar), and two CO$_2$-rich phases could form. ECO2N is capable of accurately representing thermophysical properties of CO$_2$ in a gaseous as well as in a liquid phase, but it has no provisions for modeling transitions between those phases. In ECO2N, the CO$_2$-rich phase is modeled as a single non-wetting phase that in the remainder of this paper will often be referred to as "gas," while the aqueous phase will be referred to as "liquid."

Our earlier efforts at simulating CO$_2$-brine mixtures retained much of the original EWASG formulation (Pruess and García, 2002). In particular, CO$_2$ dissolution in the aqueous phase was modeled by means of an extended Henry's law that included fugacity effects for CO$_2$ and salting-out corrections for the aqueous phase. ECO2N represents a more profound departure from this approach, as we employ newly developed correlations for the partitioning of H$_2$O and CO$_2$ between aqueous and gas phases that do not use the concept of CO$_2$ partial pressure (Spycher and Pruess, 2005).

THERMOPHYSICAL PROPERTIES

Thermodynamic conditions are specified in ECO2N with the same primary variables as in EWASG, namely (P, X$_{sm}$, X3, T) for single-phase conditions, and (P, X$_{sm}$, S$_g$+10, T) for two-phase. (When

discussing phase conditions, we refer to the fluid phases only; in all cases solid salt may precipitate or dissolve, adding another active phase to the system.) Here P is pressure, T temperature, X3 mass fraction of CO_2, and S_g gas saturation. X_{sm} pertains to the salt and denotes salt (NaCl) mass fraction X_S in the two-component H_2O-NaCl system when no solid salt is present, while it denotes solid saturation S_S+10 otherwise. The aqueous phase will in general include three components, H_2O, NaCl and CO_2. A natural choice for a salt concentration variable would be total salt mass fraction in the aqueous phase. However, using salt mass fraction in the binary system water-salt as primary variable is more convenient, as it facilitates calculation of brine properties, and treatment of salt precipitation and dissolution.

We now proceed to highlight the thermophysical property model.

Phase Partitioning

In ECO2N the mutual solubilities of CO_2 and H_2O in gas and brine phases are calculated from the correlations of Spycher and Pruess (2005). For input parameters of temperature T and pressure P, these correlations obtain the compositions of coexisting gas and brine phases in a non-iterative manner and generally within experimental accuracy in the temperature range 12 ˚C ≤ T ≤ 110 ˚C, pressures up to 600 bar, and salinity up to saturated NaCl brines. The main features of the phase partitioning are (1) CO_2 concentrations in brine increase approximately linearly with pressure at low (sub-critical) pressures, but for P > P_{crit} dissolved concentrations increase only weakly with increasing pressures; (2) water solubility in the CO_2-rich phase is substantially larger than would be predicted on the basis of an "evaporation model," that would consider water partial pressure in the CO_2-rich phase to be equal to saturated vapor pressure.

At the temperature and pressure conditions of interest to geologic disposal of CO_2, equilibrium between aqueous and gas phases corresponds to a dissolved CO_2 mass fraction in the aqueous phase, $X_{2,eq}$, on the order of a few percent, while the mass fraction of water in the gas phase, $Y_{1,eq}$, is a fraction of a percent, so that gas phase CO_2 mass fraction $Y_{2,eq} = 1 - Y_{1,eq}$ is larger than 0.99. The CO_2 mass fraction X3 in single-phase liquid conditions is restricted to X3 < $X_{2,eq}$, while for single-phase gas conditions we have X3 > $Y_{2,eq}$. Intermediate values ($X_{2,eq}$ ≤ X3 ≤ $Y_{2,eq}$) correspond to two-phase conditions with different proportions of aqueous and gas phases (Fig. 1).
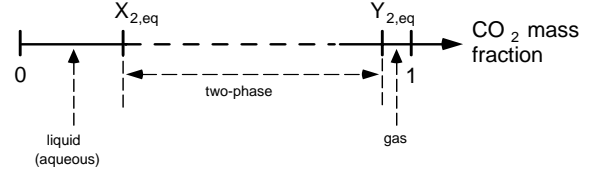

Figure 1. CO_2 phase partitioning in the system H_2O - NaCl - CO_2.

As in EWASG, the third primary variable is S_g+10 (gas saturation plus ten) in two-phase conditions. However, as a convenience to the user it is possible to initialize ECO2N with X3 in the entire range 0 ≤ X3 ≤ 1. In EWASG, specification of X3 outside the range of single-phase conditions will produce an informative message, followed by an "erroneous data initialization" error return and "stop execution." ECO2N on the other hand will proceed to internally calculate the proportions of gas and liquid phases needed to produce an overall CO_2 mass fraction X3 from the phase equilibrium constraint

$$X3\left(S_l\rho_l + S_g\rho_g\right) \;=\; S_l\rho_l X_{2,eq} + S_g\rho_g Y_{2,eq} \qquad (1)$$

and will then automatically convert the third primary variable to S_g+10. Here, ρ_l and ρ_g are the densities of liquid (aqueous) and gas phases, respectively.

An analogous scheme is applied to the second primary variable X_{sm} and the (dis-) appearance of solid salt. Salt mass fraction is restricted to the range 0 ≤ X_{sm} ≤ XEQ, where XEQ = XEQ(T) is the mass fraction of salt in NaCl-saturated brine. ECO2N accepts initialization with 0 ≤ X_{sm} ≤ 1, recognizes X_{sm} > XEQ as corresponding to presence of solid salt, and converts the second primary variable internally to the appropriate solid saturation that will result in total salt mass fraction in the binary system water-salt being equal to X_{sm}.

CO_2 Properties

Properties of pure CO_2 are obtained from correlations developed by Altunin et al. (1975). We began using Altunin's correlations in 1999 when a computer program implementing them was conveniently made available to us by Victor Malkovsky of the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) of the Russian Academy of Sciences, Moscow. Altunin's correlations were subsequently extensively cross-checked against experimental data and alternative PVT formulations, such as Span and Wagner (1996). They were found to

be very accurate (García, 2003), so there is no need to change to a different formulation.

Altunin's correlations are not used directly in the code, but are used ahead of a TOUGH2/ECO2N simulation to tabulate density, viscosity, and specific enthalpy of pure CO_2 on a regular grid of (T, P)-values. These tabular data are provided to the ECO2N module in a file called "CO2TAB," and property values are obtained during the simulation by means of bivariate interpolation. As shown in Fig. 2, the tabulation is made in such a way that for sub-critical conditions the saturation line is given by diagonals of the interpolation quadrangles. On the saturation line, two sets of data are provided, for liquid and gaseous CO_2, respectively, and in quadrangles that include points on both sides of the saturation line, points on the "wrong" side are excluded from the interpolation. This scheme provides for an efficient and accurate determination of thermophysical properties of CO_2. The ECO2N package includes a FORTRAN77 program "co2tab3.f" that implements Altunin's correlations and allows users to generate their own property tables.
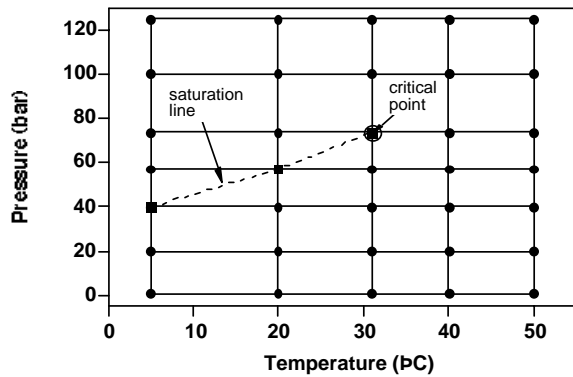

Figure 2. Schematic of the temperature-pressure tabulation of CO_2 properties. The saturation line (dashed) is given by the diagonals of interpolation rectangles.

It was mentioned above that ECO2N does not use the concept of partial pressure for the CO_2 and H_2O components in the gas phase. This makes it less straightforward to calculate thermophysical properties of the gas phase in terms of individual fluid components. We are primarily interested in the behavior of water-salt-CO_2 mixtures at moderate temperatures, T < 100 °C, say, where water vapor pressure is a negligibly small fraction of total pressure. Under these conditions the amount of water present in the CO_2-rich phase is small. Accordingly,

we approximate density, viscosity, and specific enthalpy of the gas phase by the corresponding properties of pure CO_2, without water present.

Brine density ρ_b for the binary system water-salt is calculated as in Battistelli et al. (1997). Dissolution of CO_2 causes an increase in brine density which, although small, is potentially important for the long-term fate of CO_2 plumes, as it will promote convective mixing throughout the permeable thickness of the storage aquifer (Riaz et al., 2006). ECO2N models the density of aqueous phase with dissolved CO_2 by assuming additivity of the volumes of brine and dissolved CO_2.

$$\frac{1}{\rho_{aq}} = \frac{1-X_2}{\rho_b} + \frac{X_2}{\rho_{CO2}} \qquad (2)$$

where X_2 is the mass fraction of CO_2 in the aqueous phase. Partial density of dissolved CO_2, ρ_{CO2}, is calculated as a function of temperature from the correlation for molar volume of dissolved CO_2 at infinite dilution developed by García (2001). For typical temperature conditions of interest for CO_2 storage, the molar volume of dissolved CO_2 is approximately 35 cm^3 per gram-mole, corresponding to a partial density of dissolved CO_2 of approximately 1260 kg/m^3. This is larger than brine density, which may vary between approximately 1000 kg/m^3 for pure water and approximately 1190 kg/m^3 for full halite saturation. According to Eq. (2), CO_2 dissolution will therefore cause an increase in aqueous phase density.

Fig. 3 shows the relative density increases ($\rho_1 - \rho_0)/\rho_0$ in CO_2-saturated NaCl brines as a function of salinity, calculated from the correlations used in ECO2N. Here, ρ_0 is the density of brine without dissolved CO_2, while ρ_1 is the density of brine in equilibrium with a CO_2-rich phase at prevailing conditions of (T, P). The temperature conditions in Fig. 3 correspond to depths of 1,000, 1,500, and 2,000 m, respectively, for continental crust with a typical temperature gradient of 30 °C/km and a land surface temperature of 15 °C. The data plotted in Fig. 3 were calculated for pressures that exceed hydrostatic values by approximately 20 bar, to allow for some overpressure of the stored CO_2. The relative density increase is seen to be approximately 1.1 % for pure water, and decreases by more than an order of magnitude for NaCl-saturated brines. The strong reduction of CO_2-induced density increase with increasing salinity is caused by two factors, (1) CO_2 solubility in brine decreases with increasing salinity, and (2) brine density itself increases with increasing

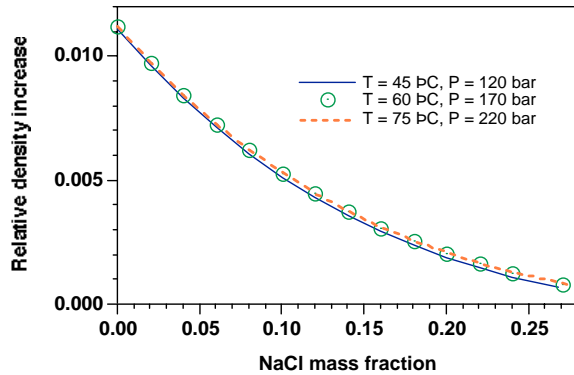salinity, so that mixing with a denser fluid (dissolved CO_2) has less of an impact.

Figure3.   Relative increase in aqueous phase density from CO_2 dissolution, as a function of salt concentration.

The correlation for brine enthalpy used in EWASG becomes inaccurate below 100 ˚C for brines of high salinity. ECO2N uses a new correlation developed by Lorenz et al. (2000) that for saturated NaCl solutions is accurate down to 25 ˚C, and to lower temperatures for less concentrated brines.

APPLICATIONS OF TOUGH2/ECO2N

An executable for the TOUGH2/ECO2N code is generated by compiling and linking the source code file eco2n.f with standard TOUGH2 V 2.0 modules, exactly like any of the other fluid property modules. A detailed discussion of ECO2N technical specifications along with illustrative applications is given in the user's guide (Pruess, 2005), which is available for free downloading on the Internet (http://www-esd.lbl.gov/TOUGH2/eco2n_info.html). The sample problems provided with ECO2N include the three saline aquifer flow problems that had been part of a recent code intercomparison study (Pruess et al., 2002, 2004). Results are generally similar to the earlier LBNL submissions to that study, but show differences in those aspects that are sensitive to water partitioning into the CO_2-rich phase. Our earlier calculations had modeled this partitioning as an evaporation process, which substantially underpredicts water uptake by the CO_2-rich phase, and thus underpredicts dry-out and precipitation phenomena.

Radial Flow from a CO_2 Injection Well

This is a basic problem of CO_2 injection into a saline aquifer, examining two-phase flow with CO_2 displacing (saline) water under conditions that may be encountered in brine aquifers at a depth of the

order of 1.2 km. A CO_2 injection well fully penetrates a homogeneous, isotropic, infinite-acting aquifer of 100 m thickness (Fig. 4), at conditions of 120 bar pressure, 45 ˚C temperature, and a salinity of 15 % by weight. CO_2 is injected uniformly at a constant rate of 100 kg/s. This problem had been included as test problem #3 in a recent code intercomparison project (Pruess et al., 2002, 2004); the full specifications are given in the ECO2N user's guide (Pruess, 2005).
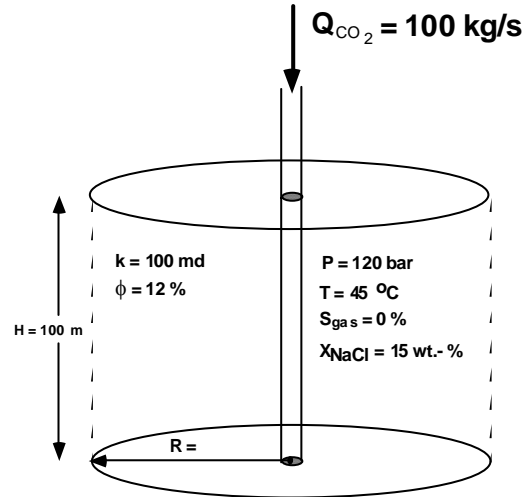

Figure 4. Schematic of radial flow problem.

The problem has a similarity property which means that the solution depends on radial distance R and time t only through the similarity variable $\xi = R^2/t$, even when taking into account all the non-linearities due to PVT properties and two-phase flow (O'Sullivan, 1981; Doughty and Pruess, 1992). Figs. 5-7 show selected results as a function of the similarity variable. Simulated water mass fractions in the CO_2-rich phase are larger by more than an order of magnitude in comparison to the evaporation model employed in our earlier simulations (Fig. 5). The Spycher and Pruess (2005) model for phase partitioning produces a more vigorous drying process, accelerating the growth of a dry-out zone around the injection well (Fig. 6), and giving rise to increased salt precipitation (Fig. 7). We note that all results submitted in the code intercomparison project by other groups also employed an evaporation model for water partitioning into the CO_2-rich phase. To facilitate comparison with earlier simulations and other codes, ECO2N retains the evaporation model as a user-selectable option. When using this option, ECO2N produces results that are virtually identical to the earlier LBNL results in the code intercomparison project.
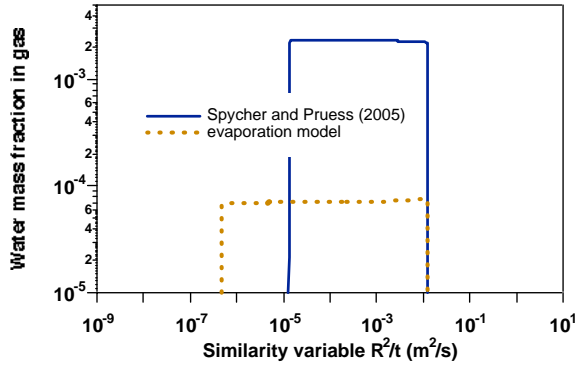
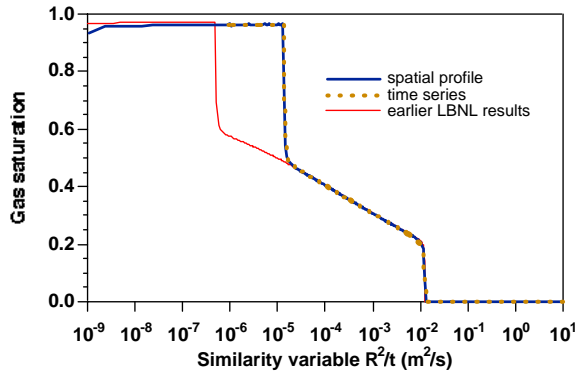*Figure 5. Simulated water mass fraction in CO$_2$-rich phase.*

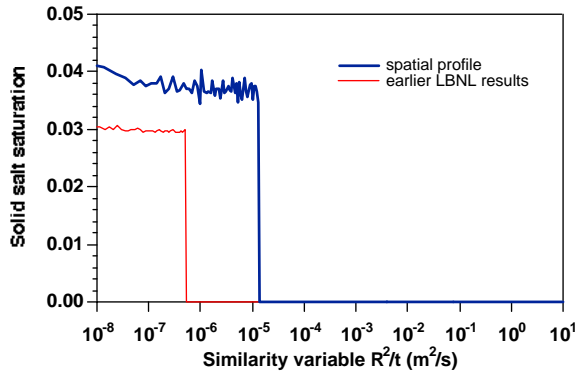*Figure 6. Simulated gas saturations.*

Figure 7. Simulated solid saturations.

Three-Phase Zone (brine-salt-gas)?

An interesting feature of our results for the radial injection problem is that precipitation of solid salt occurs only when grid blocks dry out. We do not see precipitation in the region beyond the dry-out zone, where two fluid phases, aqueous and gas, are present. Three-phase aqueous–gas–solid conditions are limited to a single grid block, moving outward with

time, at the outer boundary of the dry-out zone. This raises the question why no three-phase zone of finite thickness develops in this problem, and an additional simulation was performed to better understand the mechanism responsible for this. This additional simulation used the conditions obtained at the end of the run (8.64x10^8 s = 10,000 days) as initial conditions, except that gas saturations in the 10 outermost grid blocks of the dry-out zone, extending from R = 86.22 m to R = 107.4 m, were reduced from the calculated values of $S_g \approx 0.963$ to $S_g = 0.7$. Thus, we artificially introduced a three-phase region of approximately 21.18 m length, in which aqueous phase saturation was $S_{aq} \approx 0.963 - 0.7 = 0.263$. A continuation run was then made with all other parameters unchanged, and with the same CO$_2$ injection as before. Results for the evolution of gas and solid saturations are given in Figs. 8 and 9. It is seen that the precipitation front at the outer boundary of the three-phase zone remains stationary while the dry-out front moves outward. Precipitation in the first
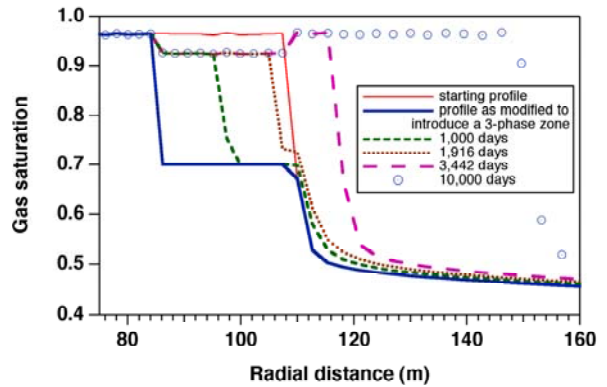

Figure 8. Gas phase saturations at different times in the region around the artificially introduced three-phase zone.
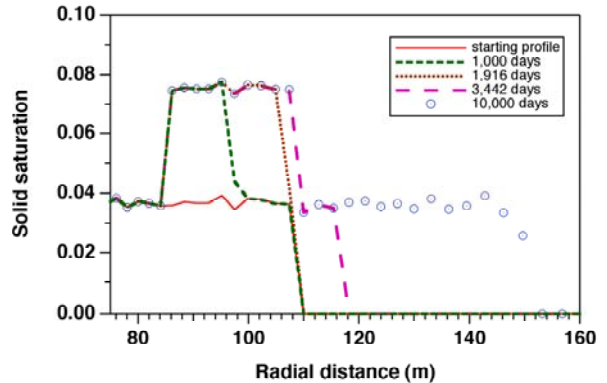

Figure 9. Solid saturations at different times in the region around the artificially introduced three-phase zone.

grid block beyond the three-phase zone occurs only after the aqueous phase has been completely removed from that block by the flowing CO_2 stream. During the time it took for the artificially introduced three-phase region to dry out ($t \approx 1.66 \times 10^8$ seconds), salt mass fraction in the fist grid block beyond the 3-phase blocks increased only slightly from initial 17.945 % to final 22.45 %, insufficient to initiate precipitation there.

The reason for this behavior can be understood in terms of water mass fraction in gas in the different regions. In the inner dried-out region, water mass fraction in gas is zero. In the three-phase aqueous-salt-gas zone beyond the dry-out zone, water mass fraction in the gas phase is approximately 2.14×10^{-3}. Beyond this is a region where the aqueous phase is at the initial salt mass fraction of 15 %, and water mass fraction in gas has a slightly larger value of approximately 2.35×10^{-3}. (Water mass fraction in gas is slightly larger there because the brine is less saline than the NaCl-saturated brine in the region with solid precipitate, so more water partitions into gas.) This means that the dry gas picks up a substantial amount of water at the inner boundary of the wet zone, but takes up only a small amount of additional water (mass fraction of 2.35×10^{-3} - 2.14×10^{-3} = 0.21×10^{-3}) when it moves from the region with solid salt to the outer region without precipitate. Thus, water removal by the flowing CO_2 stream is vigorous at the outer boundary of the dry-out zone, but only a small amount of additional water is transferred to the gas phase as it enters the region without solid salt. As a consequence, the dry-out front at the "near" (low radius) end of the three-phase zone moves outward at far greater speed than the precipitation front at the "far" end of this zone. This makes the three-phase zone self-sharpening, and prevents it from growing to finite length. The outcome is that under the conditions specified in this problem, development of a spatially extensive zone with solid salt and NaCl-saturated brine is not possible.

CONCLUDING REMARKS

ECO2N is a new fluid property module for the multiphase, multicomponent simulator TOUGH2, Version 2.0. It provides capabilities for modeling advective and diffusive flow and transport in multidimensional heterogeneous systems containing H_2O - NaCl - CO_2 mixtures. Process capabilities include coupling between fluid and heat flow, partitioning of H_2O and CO_2 among different phases, and precipitation/dissolution of solid salt. The code represents thermophysical properties of brine-

CO_2 mixtures generally within experimental accuracy for the range of conditions of interest in geologic disposal of CO_2. A fluid property table provided with ECO2N covers temperatures from ambient to 103 ˚C and pressures from ambient to 600 bar. Software to generate property tables is provided with ECO2N, making possible applications to a more extensive range of conditions. Super- as well as sub-critical conditions may be modeled, but the code currently has no provisions to treat separate liquid and gas CO_2 phases, or transitions between them.

Mixtures of H_2O - NaCl - CO_2 with phase change between liquid and gaseous CO_2 at subcritical conditions can be modeled with another fluid property module "EOSM," which includes all seven possible phase combinations in the system aqueous–liquid CO_2–gaseous CO_2 (Pruess, 2004). The development of EOSM is ongoing, and we hope to be able to release this code to the public at some future time.

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