Understanding the Multiphysical Processes in Carbon Dioxide Enhanced-Oil-Recovery Operations: A Numerical Study Using a General Simulation Framework

Shihao Wang, Colorado School of Mines; Yuan Di, Peking University; Philip H. Winterfeld, Colorado School of Mines; Jun Li and Xianmin Zhou, King Fahd University of Petroleum and Minerals; and Yu-Shu Wu and Bowen Yao, Colorado School of Mines

Summary

In this paper, we aim to enhance our understanding of the multiphysical processes in carbon dioxide (CO_2) -enhanced-oil-recovery (EOR) (CO₂-EOR) operations using a modeling approach. We present the development of a comprehensive mathematical model for thermal/hydraulic/mechanical (THM) simulation of CO₂-EOR processes. We adopt the integrated-finite-difference method to simulate coupled THM processes during CO₂-EOR in conventional and unconventional reservoirs. In our method, the governing equations of the multiphysical THM processes are solved fully coupled on the same unstructured grid. To rigorously simulate the phase behavior of a three-phase, nonisothermal system, a three-phase flash-calculation module, dependent on the minimization of Gibbs energy, is implemented in the simulator. The simulator is thus applicable to both miscible and immiscible flooding simulations under isothermal and nonisothermal conditions.

We have investigated the effect of $cold-CO_2$ injection on injectivity as well as on phase behavior. We conclude that $cold-CO_2$ injection is an effective way to increase injectivity in tight oil reservoirs and reduces overriding effect in high-water-bearing reservoirs. Using the developed general simulation framework, we have discovered and studied several intriguing multiphysical phenomena that cannot be captured by commonly used reservoir simulators, including the temperature-decreasing phenomenon near the production well and the permeability-enhancement effect induced by the thermal unloading process. These phenomena can be captured only by the fully coupled multiphysical model. The novelty of this paper lies in its integration of multiple physical simulation modules to form a general simulation framework to capture realistic flow and transport processes during CO_2 flooding, and in revealing the behavior of cold-CO₂ injection under THM effects.

Introduction

 CO_2 flooding has been a proved, effective EOR technique for secondary and tertiary oil recovery in conventional reservoirs (Zhang et al. 2018; Yang et al. 2020). The injected CO_2 has a variety of impacts on the in-situ oil/water system, including the expansion of oil volume and the reduction of oil viscosity as well as capillary forces (Grigg and Schechter 1997). During the past 3 decades, the number of active CO_2 -flooding projects in the US has increased by more than 300% (Manrique et al. 2010). CO_2 flooding has brought many waterflooded reservoirs back to life and has increased the recovery factor by up to 30%, as summarized in Rao (2001). During immiscible CO_2 flooding, CO_2 usually turns into a supercritical phase in the high-pressure/high-temperature downhole environment. The density of injected supercritical CO_2 is in general lighter than that of the in-situ hydrocarbons. Therefore, supercritical CO_2 might override oil. Meanwhile, because of the heterogeneity of the reservoir formation, viscous fingering and channeling are likely to occur in immiscible CO_2 -flooded reservoirs. Moortgat et al. (2012) noted that even a small level of local heterogeneity will lead to a significant fingering effect. Although CO_2 -EOR has achieved huge success in conventional reservoirs, it faces difficulties when applied to unconventional reservoirs. This is primarily because the extremely low permeability of unconventional reservoirs limits the injectivity of CO_2 and enhances its viscous fingering, leading to poor displacement efficiency.

From a numerical-modeling perspective, the simulation of CO₂-EOR processes mainly addresses two challenges: the fluid/rock interaction and the phase behavior of the CO₂/hydrocarbon/water system. The former has been partially addressed by the compositional relative permeability approach (Beygi et al. 2015; Yuan and Pope 2011), which is able to capture the compositional effect on the relative permeability of the three-phase system. The latter is handled in a comprehensive compositional reservoir simulation with a robust flash calculation. The compositional simulator tracks the migration of each component by means of the discretization and linearization of the governing equations. Within each solution step, the compositional simulator conducts a flash calculation to predict the phase behavior of the system. The flash calculation produces the phase combination as well as the concentration distribution at a given temperature and pressure. The first instance of flash calculation and compositional modeling for two-phase systems dates back to the 1960s (Hoffman 1968). The flash-calculation approach reported by Michelsen (1982a, 1982b) has been widely adopted, and has two steps. It first conducts a phase-stability test to determine whether a phase exists, using the work of Baker et al. (1982). It then solves the Rachford-Rice equations (Leibovici and Neoschil 1992, 1995; Okuno et al. 2010a) using Newton's iteration approach dependent on the equilibrium ratio (K-value) of each component. Although the Michelsen (1982a, 1982b) method has been successfully applied in twophase flash calculations, it has several drawbacks that cause it difficulty when applied to the three-phase flash calculation, especially in the presence of a water phase. First, Newton's iteration method used in the Michelsen (1982a, 1982b) method has convergence issues because of the discontinuity in the Rachford-Rice equation. Second, the Michelsen (1982a, 1982b) method requires multiple iterations and complex phase-stability calculations. In more recent studies, Firoozabadi and Pan (2000) and Okuno (2010a, 2010b) extended the so-called reduced model for multiphase flash calculation. The reduced model has been widely applied in gas-injection and gas/ condensate simulations because of its simplicity and effectiveness. However, the reduced model is only better than the classic K-value

Copyright © 2021 Society of Petroleum Engineers

This paper (SPE 193879) was accepted for presentation at the SPE Reservoir Simulation Conference, Galveston, Texas, USA, 10–11 April 2019, and revised for publication. Original manuscript received for review 14 February 2020. Revised manuscript received for review 19 October 2020. Paper peer approved 27 October 2020.

method when the number of components is greater than 15 to 20, which is not the usual case for actual applications. *K*-value based flash calculations have been widely adopted in the simulation of CO_2 -EOR by research codes (Pan and Oldenburg 2016) and commercial simulators (Schlumberger 2009; CMG 2010). In dealing with the convergence issue, a "hybrid" framework could be adopted for *K*-value based flash calculation, in which Newton's method is combined with the bisection method. When Newton's method fails to converge, the algorithm switches to the bisection method to search for the solution.

Besides the *K*-value approach, the minimization of the Gibbs free energy is another attractive approach for flash calculation. This approach originates from the fact that at the equilibrium state, the Gibbs free energy of the system is at its minimum. In the direct minimization of the Gibbs-energy approach, the objective function is the total Gibbs free energy of the system. By iteratively tuning the concentration distribution, this approach searches for the global minima of the objective function with Newton's method. Therefore, the flash calculation becomes an optimization problem, and global optimization techniques, such as the Branch and Bound method (Cheung et al. 2002), tunneling (Nichita et al. 2002), linear programing (Rossi et al. 2009), and the heuristic algorithm (Bonilla-Petriciolet and Segovia-Hernández 2010; Walton et al. 2011; Bhargava et al. 2013), can be used to globalize the optimization process. Zhang et al. (2011) thoroughly reviewed the global optimization techniques for the direct minimization of the Gibbs-energy method.

Compared with the *K*-value approach, the direct minimization of the Gibbs-energy method can be more easily applied to multiphase systems. Moreover, this approach is also suitable for the calculation of phase behavior in unconventional reservoirs, in which the capillary pressure has a larger effect on the phase equilibrium. In unconventional reservoirs, where the pore radius is small, the effect of capillary pressure will alter the phase behavior of the hydrocarbon/CO₂/water system (Zhang et al. 2016; Rezaveisi et al. 2018). Although it is not the focus of this work to address the alternation of phase behaviors in the confined pores, the capillary pressure can be conveniently incorporated into the Gibbs-energy approach (Rossi et al. 2009). Moreover, other physics in the unconventional reservoirs, such as the high-pressure/high-temperature environment (Rezaveisi et al. 2018) and hydrocarbon/wall interaction (Zhu et al. 2020), also have effects on the thermodynamic properties. In practice, such physical processes can be approximated by shifting the thermodynamic properties of the hydrocarbons. More rigorous approaches to include such processes into flash calculation are still under development.

Traditionally, CO_2 -EOR is modeled as an isothermal process. Thermal as well as geomechanical effects on reservoir performance have been ignored in most modeling studies of CO_2 -flooding operations. In recent years, the effect of multiphysical processes on the reservoir performance has been investigated (Rutqvist et al. 2002, 2008; Kim et al. 2012). It is reported that the THM effects on the in-situ condition induced by production/injection significantly alter the performance behavior. While the multiphysical analysis in the petroleum community mostly focuses on hydraulic/mechanical processes (Li et al. 2016; McMillan et al. 2019) and chemo/ mechanical processes (Prakash et al. 2019), the thermal/mechanical impact has been largely ignored, although it has been shown to significantly affect the production performance, especially in the vicinity of wells, in the geothermal industry (Rutqvist 1995). In particular, in a thermal unloading process (Tang et al. 2019), when cold liquids are injected into the reservoir, the injectivity of the injector should increase. In practice, the injectivity increase near the cold-water injector has been observed in geothermal reservoirs (Stefansson 1997; Kaya et al. 2011). Such phenomena could be explained by the shrinkage of rock induced by changes in the thermal stress field. Analogously in the community of CO_2 sequestration, the THM impact of cold- CO_2 injection on fracture aperture and growth has been numerically studied by Salimzadeh et al. (2018). Based on their 3D numerical studies, the fracture/fault aperture will significantly increase during cold- CO_2 injection, which is mainly because of thermal effects.

To deepen the understanding of multiphysical effects on CO_2 -EOR and explore a possible method for the recovery of tight reservoirs, we have proposed a unified THM simulation framework, named MSFLOW_CO2. We aim to demonstrate the unique and nonnegligible behavior of cold- CO_2 flooding, particularly on injectivity and sweep efficiency, which can only be observed by multiphysical simulators.

Phase Behavior and Property Calculations

In this section, we describe the numerical approach to predict the phase behaviors and rock/fluid properties during the CO_2 -flooding process. According to thermodynamic principals, at the equilibrium state, the Gibbs free energy of the system should be minimized if the surface energy induced by capillary forces is ignored. The flash calculation in MSFLOW_CO2 is based on the direct minimization of Gibbs energy, which is based on the theoretical study of Ballard and Sloan (2004) and Ballard (2002) and numerical implementation of Di et al. (2015). In this paper we briefly describe the key idea of this approach. More details are provided in Ballard and Sloan (2004), Ballard (2002), and Di et al. (2015).

The minimization of the Gibbs-energy approach is essentially to minimize the total Gibbs energy of the CO₂/hydrocarbon/water system using Lagrange optimization. The Gibbs free energy of a multicomponent system is as

where $\mu_{i\beta}$ is the chemical potential of component *i* in phase β ; $n_{i\beta}$ is the number of moles of component *i* in phase β ; N_P is the number of phases; and N_C is the number of components. In this study, $N_P = 3$. *r* is an arbitrarily chosen reference. Meanwhile, the fraction of phase β among all the phases is calculated as

$$\alpha_{\beta} = \sum_{i=1}^{N_{C}} n_{i\beta} / N_{i}\beta = 1, \dots, N_{P}; \beta \neq r, \qquad (2)$$

where N_t is the total number of moles in the whole system, as $N_t = \sum_{i=1}^{N_c} \sum_{n=1}^{N_p} n_{i\beta}$.

We then define the Lagrange function and the Lagrange multipliers as

$$G^* = G + \sum_{\substack{\beta = 1 \\ \beta \neq r}}^{N_P} \lambda_\beta \left(\alpha_\beta - \sum_{i=1}^{N_C} n_{i\beta} / N_i \right). \tag{3}$$

Downloaded from http://onepetro.org/SJ/article-pdf/26/02/918/2431723/spe-193879-pa.pdf/1 by Colorado School of Mines user on 12 September 2021

To achieve the minimum Gibbs free energy, the derivative of Eq. 3 with respect to all variables should be zero. The equilibrium ratio (*K*-value) of component *i* in phase β with respect to that in the reference phase *r* is defined as the ratio of the fugacity coefficients φ

where $c_{i\beta}$ and c_{ir} are the mole fraction of component *i* in phase β and the reference phase *r*, respectively, and $f_{i\beta}$ and f_{ir} are the fugacity of component *i* in phase β and the reference phase *r*, respectively. Following the naming convention of the petroleum industry, we use x_i and y_i to represent the mole fraction of hydrocarbon component *i* in the liquid and vapor phases, respectively. We introduce a variable θ to quantify the stability of phase β as

$$\theta_{\beta} = \ln \frac{f_{ir}}{f_{i\beta}}, \ \beta = 1, \dots, N_P. \tag{5}$$

On the basis of the equilibrium status, if phase β exists in the system, θ should be zero.

By substituting Eqs. 4 and 5 into Eq. 3, we can formulate the objective functions for each component, the details of which can be found in Di et al. (2015). We use Newton's method to iteratively minimize the objective functions. To start the iteration, the initial guess of the equilibrium ratio for the hydrocarbon component in the oil and the gas phase K_i^0 is estimated by the Wilson (1964) equation. The initial guess for the equilibrium ratio of the water component in the oil and the gas phase is set to zero. Moreover, the solubility of the hydrocarbon components in the aqueous phase is zero. We use the Soave-Redlich-Kwong equation of state to calculate the fugacity of all components in the oil and the gas phase. Helgeson's formulation (Helgeson and Kirkham 1974) is used for the prediction of the fugacity of solute in the aqueous phase, as listed in Appendix A. The formulations for calculating fluid and rock and properties, including phase relative permeability, viscosity, and stress/permeability relationship, in MSFLOW_CO2 are detailed in Appendix B. The parameters required for the flash calculation, including the binary-interaction factors, are from Pan and Oldenburg (2016), listed in Appendix C (Tables C-1 and C-2). In this work, only the CO₂ component is allowed to have a solution in the aqueous phase. Such an assumption is acceptable for most conditions in engineering practice.

Governing Equations and Numerical-Solution Approach

Governing Equations. The governing equations of the thermal/hydraulic simulation module in MSFLOW_CO2 are derived from conservation of mass and energy and describe fluid and heat transport in the porous reservoir. For a compositional system consisting of N_C components, the mass/energy-conservation equation for component *k* is

where the term *M* is the accumulation term for mass or energy, $\mathbf{F}^{\mathbf{k}}$ is the flux term, *t* is time, *q* is the sink/source term, and *k* could refer to an aqueous (water) component, a hydrocarbon component, or an energy "component." In MSFLOW_CO2, k = 1 refers to the aqueous (water) component, $k = 2, ..., N_C$ denote hydrocarbon components, and $k = N_C + 1$ denotes the internal energy. For aqueous and hydrocarbon components, the accumulation term is calculated as

$$M^{k} = \phi \sum_{\beta} S_{\beta} \rho_{\beta} x_{\beta}^{k}, \beta = L, G, A, k = 1, .., N_{C}, \qquad (7)$$

where S_{β} and ρ_{β} are the saturation and density of phase β , respectively, and x_{β}^{k} is the mass fraction of component k in phase β . Because the solubility of hydrocarbon in the aqueous phase is fairly low, we set

$$x_A^k = 0, k = 2, .., N_C.$$
 (8)

For the energy "component,"

where C_R and ρ_R are the specific heat and density of the rock, respectively, U_β is the internal energy of phase β , and T is the temperature of the system.

In Eq. 6, the flux term $\mathbf{F}^{\mathbf{k}}$ is calculated as

$$\mathbf{F}^{\mathbf{k}} = \sum_{\beta} \mathbf{F}_{\beta} \mathbf{\lambda}_{\beta}^{k} - m_{k} D_{k} \nabla y_{k}, \beta = L, G, A, k = 1, .., N_{C}, \qquad (10)$$

where D_k is the diffusive coefficient of component k in the gas phase. In the case studies of this work, D_k is set to be zero. The phase flux \mathbf{F}_{β} is calculated by the multiphase Darcy's law, as shown in Eq. 10, where K_a is the apparent permeability of the rock, $K_{r\beta}$ is the relative permeability of phase β , μ_{β} is the viscosity of β , and \mathbf{g} is the gravity vector.

$$\mathbf{F}_{\boldsymbol{\beta}} = -K_a \frac{K_{r\beta} \rho_{\beta}}{\mu_{\beta}} \big(\nabla P_{\beta} - \rho_{\beta} \mathbf{g} \big). \tag{11}$$

For the liquid and aqueous phases, K_a is identical to the absolute permeability of the rock, K_{∞} . For the gas phase, $K_a = K_{\infty}(1+b/p)$, where *b* is the Klinkenberg parameter for mixtures, which can be calculated from Wang et al. (2019a).

The energy flux has heat conduction and convection terms,

$$\mathbf{F}^{N_{c}+1} = -k_{t}\nabla T + \sum_{\beta} h_{\beta}\mathbf{F}_{\beta}, \qquad (12)$$

where k_t is thermal conductivity and h_β is the specific enthalpy of phase β .

The mechanical simulation module of MSFLOW_CO2 is based on the mean-stress method, as discussed by Wang et al. (2016). In MSFLOW_CO2, the formation rock is assumed to be a linear porothermoelastic material subject to Hooke's law,

$$\overline{\overline{\tau}} = 2G_S \overline{\overline{\varepsilon}} + \lambda_L (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \overline{\overline{I}}, \qquad (13)$$

where $\overline{\tau}$ is the stress tensor, $\overline{\epsilon}$ is the strain tensor, \overline{I} is the unit tensor, G_S is the shear modulus, λ_L is the Lamé coefficient, and ε_{ii} , k = x, y, z are the diagonal terms of the strain tensor. Eq. 13 was extended to nonisothermal materials by Nowacki (2013) and Norris (1992). Moreover, McTigue (1986) presented the porothermoelastic version of Eq. 13 as

where σ_{kk} , k = x, y, z are the diagonal terms of the stress tensor. In Eq. 14, β_T and K_B are the thermal-expansion coefficient and the bulk modulus, respectively, and ε_v is the volumetric strain, which is defined as $\varepsilon_v = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$.

By rearranging Eq. 14, we obtain

in which $\sigma_m = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ is the mean stress.

Meanwhile, the conservation of momentum for the porothermoelastic process can be described by the Navier equation (Eslami et al. 2013) as

where \mathbf{u} and $\mathbf{F}_{\mathbf{b}}$ are the displacement vector and body force, respectively. By taking the divergence of Eq. 16, we obtain

Moreover, we have the following relationship between the displacement vector and the volumetric strain,

By combining and rearranging Eqs. 16, 17, and 18, we can obtain a governing equation for the mechanical simulation,

$$\frac{3(1-\nu)}{(1+\nu)}\nabla^2\sigma_m + \nabla\cdot\mathbf{F}_{\mathbf{b}} = \frac{2(1-2\nu)}{(1+\nu)} \left(\alpha\nabla^2 P + 3\beta_T K_B \nabla^2 T\right).$$
(19)

The relationships among the mechanical moduli are,

$$E = 2G_S(1+\nu) = 3K_B(1-2\nu) \quad \lambda_L = \frac{2\nu G_S}{1-2\nu}.$$
 (20)

Numerical-Solution Approach. In MSFLOW_CO2, the governing equations are solved by the integrated-finite-difference method (Narasimhan and Witherspoon 1976). Similar to the finite-volume method, the integrated-finite-difference method divides the computational domain into gridblocks. After being integrated over gridblocks, the governing equations are converted to accumulation terms on each gridblock and flux terms on each pair of neighboring gridblocks using the Gaussian divergence theorem. The details of the integrated-finite-difference method used in MSFLOW_CO2 are as follows.

First, integrating Eq. 6 over the volume of the *n*th gridblock V_n yields

$$\frac{\partial}{\partial t} \int_{V_n} M^k \mathrm{d}V = \int_{\Gamma_n} \mathbf{F}^{\mathbf{k}} \cdot \mathbf{n} \mathrm{d}\Gamma + \int_{V_n} q^k \mathrm{d}V, \qquad (21)$$

where **n** is the normal vector and Γ is the area. The accumulation term can be then expressed as

$$\int_{V_n} M^k \mathrm{d}V = M_n^k V_n, \qquad (22)$$

where M_n^k is the discrete accumulation term of component k on gridblock n.

Meanwhile, the flux term can be expressed as

where *m* loops through all the neighboring gridblocks of gridblock *n*, and A_{nm} and \vec{F}_{nm}^{k} are the area and flux terms of component *k* between gridblocks *m* and *n*, respectively. The time derivative is approximated by the first-order finite-difference scheme. Therefore, Eq. 21 becomes

where Δt is the timestep length and l is the time level. Eq. 24 can be expressed in the residual vector form as

where **R** is the residual vector and \mathbf{x}^{l+1} is the primary variable vector, which consists of pressure, mole fraction, temperature, and mean stress at time level l+1. MSFLOW_CO2 is fully implicit and adopts an upwind weighting scheme to calculate the flux terms. Within each iteration, the linearized equation is solved by a multiscale linear solver (Wang et al. 2019b). More details of the Newton-Raphson method used in MSFLOW_CO2 can be found in Wang (2015). A summary of primary variables and secondary variables for the hydraulic, thermal, and mechanical modules of MSFLOW_CO2 is listed in **Table 1**. A flow chart that illustrates the workflow of MSFLOW_CO2 is presented in **Fig. 1**.

		Secondary Variables						
Primary Variables	Hydraulic	Thermal	Mechanical					
Pressure	Density	Equilibrium ratio	Young's modulus (constant)					
Temperature	Permeability	Thermal conductivity	Biot's coefficient (constant)					
Mole fraction	Porosity	Heat capacity	Thermal-expansion coefficient (constant)					
Mean stress	Viscosity	Fugacity						
	Saturation							

Table 1—Summary of primary and secondary variables used in MSFLOW_CO2.

Model Validation

In this section, we present model validation, including the validation of the Gibbs-free-energy-based flash-calculation module and the isothermal-fluid-flow simulation module.

Validation of Flash Calculation. We first present a seven-component hydrocarbon-mixture case and compare the vapor/liquidequilibrium ratios (*K*-values) predicted by our flash-calculation module with experimental data. The feed contains hydrogen sulfide, making it acid gas. The feed mole fraction of the seven-component acid-gas system is shown in **Table 2.** We calculate the variation of gas/liquid-equilibrium ratio at 65.56° C and at the range of reservoir-pressure variation. We compare the results with experimental data (Yarborough 1972), which is widely adopted as benchmarking data for the validation of flash calculations. The comparison is shown in **Fig. 2.** According to the comparison, our proposed flash-calculation module matches well with experimental data in the calculation of *K*-values, which validates the capability of the Gibbs-energy-based approach in handling multiphase equilibrium calculations.

Validation of Hydraulic/Mechanical Module: Mandel-Cryer Effect. In this example, we benchmark the hydraulic/mechanical module of MSFLOW CO2 with the 2D Mandel-Cryer effect. The Mandel-Cryer effect is as follows. A constant force is first applied on the two ends of a piece of saturated poroelastic rock (z-direction in our model). Then the rock is allowed to drain on the lateral sizes (x-direction in our model). It has been observed that, after the drainage starts, the pore pressure in the center of this rock will first increase before decreasing. This intriguing phenomenon was first studied by Mandel (1953) and is named the Mandel-Cryer effect. Later, Abousleiman et al. (1996) provided an analytical solution for the Mandel-Cryer effect. The physical reason behind the Mandel-Cryer effect is that the mechanical effect propagates much faster within the rock framework than the hydraulic pressure. The difference between the propagation speed causes the center of the rock frame to get compressed before the pore. The Mandel-Cryer effect is essentially a coupled hydraulic/mechanical problem and can be used for the validation of the multiphysical simulation module of MSFLOW_CO2. In this work, we adopt both structured and unstructured grids to simulate the Mandel-Cryer effect and compare the results with the analytical solution. Fig. 3 shows a conceptual model of the Mandel-Cryer effect. The initial pore pressure is set to be 2.2 MPa. The porosity of the rock is 0.2. The water viscosity is set to be 0.001 Pa·s (1 cp). Young's modulus, Poisson's ratio, and the Biot coefficient is 15.0 GPa, 0.3, and 1.0, respectively. The permeability of the rock is 1 md. To demonstrate the capability of MSFLOW_CO2 in handling an unstructured grid system, given a 1×1 -m computational domain, we have created a Voronoi grid with 400 gridblocks using an open-source program developed by Park (2019). For the convenience of comparison, the unstructured grid is created as follows. 20×20 uniformly distributed points (also called "seeds") are first put into the square domain. Each seed is then shifted randomly by $0.001 \times L$, where L is the length of the domain. The Voronoi grid is then generated from the seeds using the Reem (2009) algorithm. We have also generated a 20×20 structured grid to compare with the results of the unstructured grid. Our simulation consists of two steps. At first, we only apply the compressive force (5 MPa) on the rock for a sufficiently long time (2 years in this case). We then allow the rock to drain on the lateral sizes and record the change of the pore pressure in the center of the rock. The drainage process is simulated as a constant-pressure boundary condition with the initial pressure (3.3 MPa). The variation of the pore pressure in the center of the rock is shown in Fig. 4, according to which our numerical results of both the structured grid and unstructured grid both match the analytical solution very well. This case study validates the multiphysical simulation of MSFLOW CO2.

Validation of Thermal/Hydraulic Module: Heat Sweep of a Vertical Fracture. In this subsection, we validate the thermal/hydraulic simulation module of MSFLOW_CO2 with the commercial nonisothermal reservoir simulator CMG STARSTM (CMG 2010). We simulate the nonisothermal problem of injecting cold liquid into a vertical fracture, which is initially of in-situ reservoir temperature. This problem was first investigated by Pruess and Bodvarsson (1984) in a geothermal reservoir. We compare the results of MSFLOW_CO2 with the thermal/hydraulic module of CMG-STARS. In a given vertical fracture sandwiched by semi-infinite half-spaces of impermeable rock, we set a cold-liquid injector and a constant-pressure producer at the two ends of it, as shown in Fig. 5. The fracture is bounded by semi-infinite half-spaces of impermeable rock, which serve as a heat-supply source. The initial temperature of the fracture is 100°C. Cold water of 51°C is injected at a constant rate of 3.75 kg/s. The water is produced at 10 MPa. The matrix rock is discretized into $20 \times 20 \times 20 \times 20$ -m gridblocks. The fracture is discretized into $20 (x) \times 20$ -m (y) and 0.04-m (z) gridblocks. The permeability and the porosity of the fracture is 200 darcies and 0.2, respectively. The heat conductivity, specific heat, and rock-grain density of the system are $2 \text{ W/m} \,^\circ\text{C}$, 1000 J/kg $\,^\circ\text{C}$, and 2600 kg/m^3 , respectively. Initially the pressure at the top of the system is 25 MPa. The pressure at the other portion is calculated through hydraulic equilibration. We simulate the system for 1×4 days. The temperature field of the fracture

plane at the end of the simulation is shown in the left of **Fig. 6**. The lower part of the fracture tends to be cooler than the upper part, which indicates that cold fluids become denser and tend to accumulate at the bottom. The comparison of the temperature of the pro-duced fluid between MSFLOW_CO2 and CMG-STARS is shown in the right of Fig. 6. According to the comparison, the results of MSFLOW_CO2 match those from the commercial simulator very well.



Fig. 1—Flow chart of MSFLOW_CO2.

Component	Feed Mole Fraction (%)
CH ₄	77.43
C ₂ H ₆	5.74
C ₃ H ₈	2.99
<i>n</i> -C ₅ H ₁₂	4.66
<i>n</i> -C ₇ H ₁₆	3.59
<i>n</i> -C ₁₀ H ₂₂	2.63
H_2S	2.96

Table 2—Feed mole fraction of a seven-component acid-gas system.



Fig. 2—Comparison with laboratory-measured gas/liquid-equilibrium factor at 65.56°C.



Fig. 3—Conceptual model of the Mandel-Cryer effect case: (left) structured grid; (right) unstructured grid. The red point is where pressure variation is monitored and compared.

Applications

Case 1: Compaction and Low-Temperature Effects. In this subsection, we investigate the effects of the compaction and temperature change on the rock permeability and apparent gas permeability. The compaction effect is essentially the stress change induced by fluids produced from the reservoir. The low-temperature effect is the stress change from cold-liquid injection into the reservoir. The absolute permeability is calculated from porosity using equations in Appendix B (Eq. B-8). The input parameters used for this study are listed in **Table 3.** The variations of rock absolute permeability and porosity with respect to pressure and temperature reduction. If the reservoir temperature decreases from 100 to 20°C, the permeability rapidly increases. Meanwhile, the absolute permeability is also sensitive to pressure changes. However, in practice, the pressure changes in the reservoir will not be too large, subject to the limitation of the facilities.

We further argue that the cold water can reduce the capillary pressure because of thermal/mechanical effects, and therefore reduce the imbibition effect. According to the Young-Laplace equation, the surface tension or the surface energy will increase as temperature decreases. At the same time, the pore-throat radius or size will also increase as the temperature drops down because of the shrinkage of rock grain or solids induced by the change of the thermal stress. In the following work, we aim to quantify the low-temperature effect. The Leverett (1941) formulation is used to calculate the capillary pressure, as shown in Eq. B-9. We use the Kozeny-Carman equation

$$P_{c} = P_{c0} \frac{(1 - \phi_{0})\phi_{0}}{(1 - \phi)\phi}.$$
 (26)



Fig. 4—Comparison of the pressure variation at the center of the bulk among the analytical solution and simulation results of the structured grid case and the unstructured grid case.



Fig. 5—(Left) Conceptual model of the heat-sweep case study; (right) fracture plane with the locations of injection as well as production.



Fig. 6—(Left) Temperature profile of the fracture plane at the end of the simulation; (right) temperature of the produced fluids.

Note that the Leverett (1941) correlation is dependent on isothermal conditions. To take the temperature effect into consideration, we should also include the change of surface tension in our analysis. The surface-tension profile is shown in **Fig. 8.** According to the results, when the temperature decreases from 110 to 60° C, the surface tension increases by approximately 20%.

We use Eq. B-6 to calculate the porosity (Rutqvist et al. 2002). In Eq. B-6, a is an experimental parameter that quantifies the mechanical sensitivity of the rock. The change of σ' is calculated by

$$\Delta \sigma' = \beta K_B (T - T_{\rm ref}), \qquad (27)$$

$$\gamma_D = \frac{P_c(T)}{P_c(T)}$$

where T_{ini} , the original reservoir temperature, is set as 110°C. We let the reservoir temperature decrease from 110 to 60°C and plot γ_D vs. temperature in **Fig. 9.** The parameters used in this analysis are listed in **Table 4.**

Properties	Values	Units
Linear thermal-expansion coefficient	11.2	10 ^{−6} m/(m·K)
Young's modulus, <i>E</i>	12.0	GPa
Poisson's ratio, v	0.25	Dimensionless
Initial permeability, k_0	0.001	md
Biot's coefficient, α	1.0	Dimensionless
Residual porosity, ϕ_r	0.009	Dimensionless
Zero-stress porosity, ϕ_0	0.1	Dimensionless
Reference temperature, $T_{\rm ref}$	100	°C
Reference pressure, P _{ref}	20	MPa

Table 3—Parameters used in the analysis of compact and low-temperature effects.



Fig. 7—Variations of rock absolute permeability and porosity with respect to pressure and temperature change: (left) absolute permeability; (right) porosity.



Fig. 8—Surface tension of water vs. reservoir temperature. Note that the reservoir temperature (x-axis) is in the reverse sequence.



Fig. 9—(Left) Capillary pressure ratio vs. reservoir temperature with different Young's modulus. (Right) Capillary pressure ratio vs. reservoir temperature with different stress coefficient (parameter *a* in Eq. B-6).

Properties	Values	Units
Initial porosity of the matrix	0.02	Dimensionless
Linear thermal-expansion coefficient	11.2	10 ⁻⁶ m/(m·K)
Young's modulus, <i>E</i>	12.0	GPa
Poisson's ratio, v	0.25	Dimensionless
Biot's coefficient, α	1.0	Dimensionless
Residual porosity, ϕ_r	0.009	Dimensionless
Zero-stress porosity, ϕ_0	0.15	Dimensionless
In-situ reservoir mean stress, σ'	20	MPa

Table 4—Parameters used in the analysis of capillary behavior.

According to the results, as the reservoir temperature decreases from 110 to 60° C, the capillary pressure decreases by 20 to 40%. For the rocks that are more sensitive to change of thermal stress (with higher bulk modulus), the low-temperature effects are more significant. Moreover, the thermal effect on the porosity is dominant compared with the effect on the surface tension, leading to decreasing capillary pressure with respect to decreasing temperature. The reason for such a phenomenon can be seen by comparing the trend of surface tension (in Fig. 8) with the porosity (in the right-hand image of Fig. 7). When reservoir temperature decreases by 50° C, the surface tension increases by only 20%, while the porosity decreases by more than 200%. In general, the surface tension has an approximately linear relationship with the temperature, while the porosity is an exponential function of the temperature, especially for stress-sensitive tight reservoirs.

Case 2: Simulation of Cold-CO₂ Immiscible Flooding in Tight Rock Reservoirs. In this case, we present the study of cold-CO₂ injection in tight rock reservoirs. We use authentic rock-property data from Sulige reservoir. Cold CO₂ is injected at a rate of 0.3 kg/s into a 102×102 -m reservoir for 3 years. One production well is producing at a constant bottomhole pressure (BHP) of 16.2 MPa. The initial temperature of the reservoir is 85° C. The conceptual model of this case is shown in **Fig. 10**. To monitor and understand the flow behaviors, we set a point of observation in the center of the conceptual reservoir, which is represented by a black dot in Fig. 10. The three-phase relative permeability is calculated using the extended Brooks-Corey model (Delshad and Pope 1989). The initial distribution of components is shown in **Table 5**. The other input parameters, including the initial phase saturation, which is calculated by the initialization module, are listed in **Table 6**. We run three cases in which the injection temperatures (temperature of CO₂ when it arrives at the formation) are 20, 40, and 60° C, respectively. The domain is discretized uniformly into 51×51 gridblocks. **Fig. 11** shows a comparison of the phase behavior of CO₂/propane/decane, which mimics a mixture consisting of CO₂, an intermediate component, and a heavy component at different temperature conditions. In the immiscible system studied by this case, injected CO₂ becomes supercritical and tends to accumulate in the gas phase; hence, it is labeled as a "gas" phase in the flash-calculation module. As demonstrated by the comparison, when the system temperature decreases, the percentage of hydrocarbon in the gas phase becomes lower; therefore, a miscible condition is more likely to be achieved for cold-gas-injection operations.

We first qualitatively show the THM effects of cold-liquid injection. The distribution of gas-phase saturation and temperature after 1 year of injection is shown in **Fig. 12.** According to the gas-phase-saturation field, the gas-phase saturation increases near the injector. Therefore, this is immiscible flooding. Moreover, the gas saturation decreases in certain region near the saturation front. This is because the pressure effect propagates faster than the saturation effect. The buildup of pressure decreases the gas saturation in the region near the saturation front. According to the temperature field, the temperature in the vicinity of the producer slightly decreases. The reduction of the temperature is because the energy of the system is consumed by the expansion of the in-situ fluids, known as the Joule-Thomson effect. From this phenomenon, we can conclude that our simulator is capable of capturing many aspects of the complex THM behaviors of the multiphysical system. The variation of scaled permeability (transient permeability to initial permeability) at the injector with respect to time is shown in the left of **Fig. 13**, according to which the injected cold CO₂ effectively increases the injectivity near the injector. When the injection temperature decreases from 60 to 20° C, the eventual increase of the permeability increases from 170 to 280%. From this observation, it can be concluded that cold-CO₂ injection can be adopted to improve the EOR performance of unconventional reservoirs. The variation of gas-phase saturation with different injection temperatures at the observation point located at the center of the reservoir is shown in the right of Fig. 13. From Fig. 13, the gas-phase saturation of the three cases all decrease before increasing, subject to the pressure-propagation effect, as mentioned previously. Moreover, the minimal values of the gas saturation of

the three cases are not the same. Two competing physical processes can be identified in this regard. On one hand, when injection temperature is higher, the pressure at the injector's end builds up more significantly, which tends to reduce the gas-phase saturation and to increase the liquid-phase situation. On the other hand, when the injection temperature becomes higher, the solubility of lighter components including CO_2 and methane decreases, resulting in incremental gas-phase saturation. As a brief summary, the preceding analysis demonstrates not only the complexity of the multiphysical processes emerging in cold- CO_2 injection, but also the necessity of developing THM simulators.



Constant-BHP producer

Fig. 10—Conceptual model of the cold-CO₂ immiscible flooding case: (left) bird view of the reservoir and (right) grids of the model.

Component	Formula	Mole Fraction
Methane	CH_4	0.16736
Ethane	C ₂ H ₆	0.04885
<i>n</i> -Heptane	C ₇ H ₁₆	0.09334
n-Nonane	C ₉ H ₂₀	0.05751
<i>n</i> -Decane	C ₁₀ H ₂₂	0.33736
Carbon dioxide	CO ₂	0.05854
Water	H ₂ O	0.23704

Table 5—Initial distribution of component for cold-CO2 immiscible flooding case.

Property	Value	Unit
Young's modulus	26	GPa
Poisson's ratio	0.25	Dimensionless
Linear thermal-expansion coefficient	11.2	10 ^{−6} m/(m⋅K)
Rock permeability	0.2	md
Residual porosity, ϕ_r	0.02	Dimensionless
Zero-stress porosity, ϕ_0	0.2	Dimensionless
Stress coefficient, a	2×10 ⁻⁸	Dimensionless
Gridblock length	2	m
Injection temperature	50	°C
Initial temperature	85	°C
Initial pressure	35.2	MPa
Production pressure	16.2	MPa
Initial mean stress	80.6	MPa
Initial gas saturation	0.382	Dimensionless
Initial oil saturation	0.518	Dimensionless
Initial water saturation	0.1	Dimensionless
Residual gas saturation, S_{gr}	0.1	Dimensionless
Residual oil saturation, S_{or}	0.1	Dimensionless
Residual water saturation, Swr	0.1	Dimensionless

Table 6—Input parameters for cold-CO₂ immiscible flooding case.



Fig. 11—Gas-phase mole fraction of CO_2 /propane/decane system at different pressure/temperature conditions: (left) 20°C and 40 MPa and (right) 60°C and 40 MPa.



Fig. 12—Gas-phase saturation and temperature distribution after 1 year of injection (injection temperature = 60°C).



Fig. 13—(Left) Variation of scaled permeability at the injector with respect to time. (Right) Variation of gas-phase saturation at the observation point.

On the basis of the qualitative analysis discussed, we take a further step to quantitatively analyze the effect of the THM process on the injectivity. Because of the low in-situ permeability of tight rock formations, the BHP usually builds up rapidly, which limits the injection rate as well as the sweeping efficiency. Hence the control of BHP is of great importance to the success of gas EOR in tight formations. One solution for this issue is adopting a huff 'n' puff strategy (Abedini and Torabi 2014). In this work, we argue that the BHP can be effectively controlled by $cold-CO_2$ injection, taking advantage of the thermal unloading effect. We next compare the BHP and recovery factor with and without the consideration of the THM effect by running two cases with injection temperatures of 20 and 85°C (equal to reservoir temperature), respectively. The recovery factor in this case is defined as the ratio of recovered mass of hydrocarbons with respect to the initial in-place mass of hydrocarbons. We set a field-management strategy as follows. In the beginning, the simulator first honors the initial injection rate of 0.3 kg/s. When the BHP increases by 40 MPa (approximately 110%), which exceeds the maximum tolerance of the downhole facilities, the injector switches to honor the maximum BHP. We compare the varying BHP and the recovery factor with and without the THM effects during the period of the 1,000-day injection, as shown in **Fig. 14.** According to the results, without the considerations of the multiphysical effects, the BHP at the injector rapidly increases to the maximum allowable value, which prevents further injection. The injection rate thus drastically decreases. Such a phenomenon implies that the injected CO_2 cannot propagate far into the reservoir because of the low permeability of the formation. The injected CO_2 accumulates in the vicinity of the injector, causing the BHP to rapidly increase, resulting in low sweeping efficiency. In contrast, with the THM effects, the BHP grows much slowly. At approximately Day 380, the BHP starts to drop, indicating that the injector starts to "feel" the pressure drop induced by the producer. Such a phenomenon results from the fact that the injected cold liquid enhances the injectivity of the injecting well. The thermal unloading effect promotes the sweeping efficiency, leading to an 11% increase of RF improvement in this synthetic case study. Another interesting phenomenon we observe is that at the time between Days 40 and 50, the production rate without the THM effects is slightly higher than that with the THM effect, as shown in the right-hand side of Fig. 14. This is because the sudden increase of BHP at the injector creates a "kick" to the pressure field, causing the flow rate to slightly increase. It is still an open question to us whether such a process is physical or is caused by numerical dispersion.



Fig. 14—Comparison of the BHP of the injector and the recovery factor of the reservoir with and without the consideration of the multiphysical effects during the EOR process.

Case 3: Simulation of Cold-CO₂ Miscible Flooding in High-Water-Bearing Reservoirs. If an oil reservoir is in the vicinity of an aquifer or has been waterflooded, the water content in the reservoir will be relatively high, and the solution of CO_2 in the aqueous phase cannot be ignored in a numerical simulation. Such a process is complicated by the THM effects during cold-CO₂ flooding. In this case study, we investigate the multiphysical effect of cold-CO₂ injection in a reservoir with a high bottomwater level. We simulate a 3D case with one cold-CO₂ injector and one producer, which produces at a constant BHP of 20 MPa. In the horizontal plane, the length of the reservoir along the *x*- and *y*-direction is 150 m, respectively. We discretize the reservoir into 50×50 uniform gridblocks. The thickness of the reservoir is 60 m. Along the vertical direction, the reservoir is discretized into 10 uniform layers. The injection well and production well are located at Cells (1, 1, 6) and (50, 50, 6), respectively. The initial distribution of hydrocarbon components in the oil phase is listed in **Table 7.** The parameters of this case are listed in **Table 8.** The parameters of the relative permeability curves are the same as those used in the immiscible flooding case. At the injection condition, the injected CO₂ is miscible at the first contact with the in-situ oil; therefore, the case under study is miscible flooding. The CO₂-enriched phase is thus labeled as the "oil" phase.

Component	Formula	Mole Fraction
Methane	CH ₄	0.150
Ethane	C_2H_6	0.100
n-Pentane	C_5H_{12}	0.100
n-Heptane	C ₇ H ₁₆	0.100
n-Octane	C_8H_{18}	0.250
<i>n</i> -Decane	C ₁₀ H ₂₂	0.300

Table 7—Initial distribution of hydrocarbon components in the oil phase at the top of the reservoir for $cold-CO_2$ miscible flooding case.

In such a reservoir, the oil mobility drops rapidly from the top to the bottom of the reservoir. It can be expected that without the alteration of the rock permeability, the injected CO_2 will tend to accumulate in the top part of the reservoir because of its low density, causing the CO_2 -overriding effect. In this case we demonstrate how cold injection can potentially compensate the overriding effect. We first set up the initial state of the reservoir by capillary/gravity equilibrium. The relationship between the capillary pressure and the oil saturation is shown as the blue curve in the left-hand side of **Fig. 15**. We set the bottom layer of the reservoir as the datum layer, of which the pressure is 40 MPa and oil saturation is at the irreducible oil saturation. The pressure and oil saturation of the reservoir are calculated using the gravity difference between the oil and water phase, which is compensated by capillary pressure. To fulfill the equilibrium calculation, we set the volume of the bottom to be infinitely large and apply the same mole concentration to the whole reservoir. We shut the wells and let the reservoir system equilibrate by itself for a sufficiently long time (100 years in this case) and take the resulting pressure gradient as the initial condition for the case study. The calculated initial oil saturation is shown in the left-hand side of Fig. 15. A 3D view of the initial oil-saturation field along with the grid system is shown in the right-hand side of Fig. 15.

The simulation is run for 1,500 days. The oil-saturation, temperature, and rock-permeability fields at the end of the cold- CO_2 injection period are shown in **Fig. 16**. It can be seen that the part of the reservoir where permeability increases highly correlates with the region that is swept by the CO_2 -rich phase, indicating that the thermal unloading effect significantly enhances the mobility of the system. To further demonstrate the multiphysical effect, we simulate a case where the injection temperature is identical to the reservoir pressure and compare it with the cold-injection case. As a comparison, the CO_2 -rich oil saturation at the end of the injection with injection temperature of $100^{\circ}C$ is shown in **Fig. 17**. According to the comparison, the cold-injection case has significantly less overriding

phenomenon, the reason of which lies in the following two aspects. On one hand, the density as well as the viscosity of the injected CO_2 is relatively higher in the low-temperature environment, and the buoyancy effect is therefore less prominent in the cold-injection case. On the other hand, because the permeability is substantially enhanced in the vicinity of the injection point, which is located in the lower one-half of the reservoir, the liquid phase thus preferably flows in the lower part of the reservoir. The two overlapping causes of cold- CO_2 injection effectively diminish the overriding effect, resulting in better sweeping efficiency. These results also indicate that in the cold- CO_2 -injection scenario, the injection point should be at the lower one-half of the reservoir to compensate the overriding effect. Because cold- CO_2 injection is able to improve the rock permeability, the injection point should not be selected in highly permeable layers to avoid channeling-induced early CO_2 breakthrough. A similar phenomenon has been observed in the numerical study of geothermal reservoirs (Wang et al. 2016). Moreover, according to the temperature profile, the temperature in the vicinity of the producer shows no significant reduction compared with the immiscible flooding case, which is because the liquid phase is less compressible than the gas phase and the Joule-Thompson effect is thus not visually observed.

Property	Value	Unit
Young's modulus	22	GPa
Poisson's ratio	0.25	Dimensionless
Rock permeability	4	md
Biot's coefficient	1.0	Dimensionless
Linear thermal-expansion coefficient	11.2	10 ^{−6} m/(m·K)
Residual porosity, ϕ_r	0.02	Dimensionless
Zero-stress porosity, ϕ_0	0.15	Dimensionless
Stress coefficient, a	2×10 ⁻⁸	Dimensionless
Reservoir initial temperature	100	°C
Datum pressure	40	MPa
Datum depth	-57	m
Production pressure	20	MPa
Injection rate	0.7	kg/s
Initial mean stress	85	MPa
Residual oil saturation, Sor	0.15	Dimensionless
Irreducible water saturation, S_{wr}	0.12	Dimensionless

Table 8—Input parameters for cold-CO₂ injection case.







Fig. 16—Distribution of the oil saturation, temperature, and rock permeability at the end of cold-CO₂ injection.



Fig. 17—Oil-saturation profile at end of injection; injection temperature = 100°C (reservoir temperature).

We select Cells (25, 25, 6) as an observation point, which is located at the center of the injection layer. The comparison of the CO_2 -rich oil phase saturation and the total concentration of CO_2 component at the observation point with and without the multiphysical effect is shown in **Fig. 18**. According to the results, the multiphysical effect induced by cold injection significantly mobilizes and advances the propagation of the oil phase. An intriguing phenomenon from Fig. 18 is that the oil saturation has a short decline when the CO_2 front reaches the observation point. This phenomenon is resulted from the solution of CO_2 in the aqueous (water) phase. To highlight the effect of CO_2 solubility, we simulate a case with no CO_2 solution. We do so by manually eliminating the calculation of the Shock and Helgeson (1988) formulation. The comparisons of the oil saturation, CO_2 total concentration, and oil-phase viscosity are shown in **Fig. 19**. According to the comparison, when CO_2 only exists in the oil phase, the variation of the oil-phase saturation become monotonous. It can then be concluded that for each individual gridblock, the CO_2 flooding in this model consists of three stages. In the first stage, before the CO_2 front reaches the cell, the inflowing hydrocarbon is mostly because of the mobilization and expansion of the oil phase in the upstream direction. In the second stage, the CO_2 component reaches the targeted gridblock, and the oil phase competes with the aqueous phase in the solution of the CO_2 component. In the third stage, the inflowing oil phase eventually consists of the pure- CO_2 component. For Cells (25, 25, 6) with cold injection, the three stages are roughly between Days 0 to 500, 500 to 1,000, and 1,000 to 1,500, as shown in Fig. 18.



Fig. 18—(Left) Comparison of oil-saturation variation at Cells (25, 25, 6) at different injection temperature and (right) comparison of CO₂-concentration variation at Cells (25, 25, 6) at different injection temperatures.



Fig. 19—Comparison of property variation at Cells (25, 25, 6) with and without the CO₂ solution in the aqueous phase: (left) oilsaturation variation, (middle) CO₂ concentration, and (right) oil viscosity.

We further investigate the grid-size effect on the simulation result as well as computational efficiency, which is quantified by central-processing-unit (CPU) times. On the basis of the base model (Case 1), we run two more cases. All three cases are run by an Intel® CoreTM i7-7700 processor (Intel Corporation, Santa Clara, California, USA). In the first one of the two cases, we refine the vertical direction of the grid by two times, so that the grid becomes $50 \times 50 \times 20$. Along the vertical direction, the gird size is 3 m. In another

case, we refine the grid along the x- and y-direction into 100×100 blocks. The detailed model descriptions of the three cases, along with their CPU time performances, are summarized in **Tables 9 and 10**. According to Table 10, for all three cases the CPU time spent in the flash-calculation module is steadily between 20 and 30%, while the portion of CPU times spent in the linear solver increases along with model size. The comparison of the CO₂ total concentration at the end of the injection is presented in **Fig. 20**. According to the comparison, Case 1 (the base case) and Case 3 yield roughly close (within 10%) results, while the result of Case 2 is different from the others. An interesting finding from the comparison is that Case 2 requires the most computational resources, although it has fewer gridblocks than Case 3. This phenomenon implies that in such a case with vertical-density instability, refining along the vertical direction is critical for improving the accuracy of the simulation results.

Case Index	Number of Grids, <i>x</i> -Direction (m)	Number of Grids, <i>y</i> -Direction (m)	Number of Grids, z-Direction (m)	Total Gridblocks	Block Size (m×m×m)
Case 1	50	50	10	25,000	$3 \times 3 \times 6$
Case 2	50	50	20	50,000	$3 \times 3 \times 3$
Case 3	100	100	10	100,000	$1.5\times1.5\times6$

Table 9—Summary of model dimensions for comparison of grid sizes.

Case Index	Linear Solver (days)	Flash Calculation (days)	Miscellaneous Items (days)	Total CPU Time (days)
Case 1	0.06	0.03	0.05	0.14
Case 2	0.37	0.24	0.25	0.86
Case 3	0.31	0.20	0.18	0.69

Table 10—Comparison of CPU time.



Fig. 20—Comparison of the CO₂ total concentration at the end of the injection: (left) $50 \times 50 \times 10$; (middle) vertically refined to $50 \times 50 \times 20$; (right) horizontally refined to $100 \times 100 \times 10$.

Conclusions

 CO_2 injection has been among the few options for effective improved-oil-recovery/EOR operations for both conventional and unconventional oil reservoirs under current economic conditions. Even with the significant progress made in modeling studies of CO_2 -EOR processes in the past several decades, many important physical processes, such as geomechanics and thermal influence, are still poorly understood or largely ignored. To study the effects of THM processes on CO_2 -EOR performance, this paper presents a comprehensive mathematical model to simulate multiphysical THM flow and transport processes in reservoirs using an unstructured grid. We have implemented a fully coupled THM framework model in MSFLOW_CO₂ to simulate the multiphysical processes during CO_2 -EOR. The THM modules of the developed model have been verified against analytical and numerical solutions with sufficient accuracy. The mean-stress method used in this simulator for geomechanics coupling is able to capture the poroelastic effect during the CO_2 -EOR processes in petroleum reservoirs.

To simulate the complex phase behaviors of the three-phase system, we have implemented an efficient flash-calculation module that uses minimization of the Gibbs free energy. We have benchmarked the flash-calculation module with respect to experimental results. The minimization of the Gibbs free energy shows the flexibility in capturing the phase transition during CO₂ flooding. Moreover, this method can be potentially applied to simulate more complex systems, such as systems with four or more phases.

As application examples, we have studied the effects of miscible and immiscible $cold-CO_2$ injection on the production performance of unconventional reservoirs. This effect has been ignored in general by existing commercial simulators or modeling studies. We have discovered that $cold-CO_2$ injection effectively increases the injectivity in CO_2 application in low-permeability unconventional reservoirs. The approaches and results presented in this work can potentially provide insights to field applications of CO_2 EOR operations.

Nomenclature

- $A = area of a connection, m^2$
- $D = diffusive coefficient, m^2/s$
- E = Young's modulus, Pa
- $f_i =$ fugacity of the *i*th component, Pa
- F =flux term, mole/second

Downloaded from http://onepetro.org/SJ/article-pdf/26/02/918/2431723/spe-193879-pa.pdf/1 by Colorado School of Mines user on 12 September 2021

- G =Gibbs energy, J
- $G^* =$ Gibbs energy for optimization, J
- G_S = shear modulus
- h = enthalpy
- K_a = apparent permeability, m²
- K_i = equilibrium ratio of component *i*, dimensionless
- K_r = relative permeability, dimensionless
- K_R = formation heat conductivity, W/(msK)
- K_{β} = phase heat conductivity, W/(msK)
- K_{∞}^{p} = absolute permeability, m²
- M = accumulation term, mole
- n = number of moles, mole
- Nc = number of components, dimensionless
- N_P = number of phases, dimensionless
- Nt =total number of moles, mole
- P =pore pressure, Pa
- Pc = capillary pressure, Pa
- P_{CR} = critical pressure, Pa
- Pr = reduced pressure, Pa
- Q = generation term, mole/second
- \mathbf{R} = residaul vector, dimensionless
- S_{β} = phase saturation, dimensionless)
- T = temperature, K
- T_{CR} = critical temperature, K
- Tr = reduced temperature, K
- $T_{\rm ref} =$ reference temperature, K
 - t = time, seconds
 - $\mathbf{u} = displacement vector, m$
- u_{β} = phase specific internal energy, J/mole
- $\dot{V} =$ volume, m³
- x_i = mass concentration of the *i*th component, dimensionless
- z_i = mole fraction of the *i*th component, dimensionless
- $\alpha = Biot's$ coefficient, dimensionless
- α_{β} = mole fraction of phase β , dimensionless
- $\beta =$ phase index
- β_T = thermal expansion coefficient diagonal strain component, dimensionless
- $\Delta t =$ length of time step, seconds
- $\varepsilon_v =$ volumetric strain, dimensionless
- θ_{β} = stability indicator of phase β , dimensionless
- λ'_L = Lame's coefficient, Pa
- $\lambda_{\beta} =$ Lagrange multiplier, dimensionless
- $\mu = \text{viscosity}, \text{Pa} \cdot \text{s}$
- μ_i = chemical potential of the *i*th component, J/mole
- $\rho = \text{molar density, mole/m}^3$
- $\sigma' = \text{effective stress}, \text{Pa}$
- σ_{kk} = diagonal stress component
- $\sigma'_m =$ effective mean stress, Pa
- σ_m^m = mean stress
- $\phi = \text{porosity}, \text{dimensionless}$
- $\varphi =$ fugacity coefficient, dimensionless

Acknowledgments

The authors at the Colorado School of Mines would like to thank Energi Simulation for their financial support.

References

- Abedini, A. and Torabi, F. 2014. Oil Recovery Performance of Immiscible and Miscible CO₂ Huff-and-Puff Processes. *Energy Fuels* **28** (2): 774–784. https://doi.org/10.1021/ef401363b.
- Abousleiman, Y., Cheng, A. D., Jiang, C. et al. 1996. Poroviscoelastic Analysis of Borehole and Cylinder Problems. Acta Mechanica 119 (1-4): 199-219. https://doi.org/10.1007/BF01274248.
- Baker, L. E., Pierce, A. C., and Luks, K. D. 1982. Gibbs Energy Analysis of Phase Equilibria. SPE J. 22 (5): 731–742. SPE-9806-PA. https://doi.org/ 10.2118/9806-PA.
- Ballard, A. L. 2002. A Non-Ideal Hydrate Solid Solution Model for a Multi-Phase Equilibria Program. PhD dissertation, Colorado School of Mines, Golden, Colorado, USA (May 2002).
- Ballard, A. L. and Sloan, E. D. 2004. The Next Generation of Hydrate Prediction: Part III. Gibbs Energy Minimization Formalism. *Fluid Phase Equilib* **218** (1): 15–31. https://doi.org/10.1016/J.FLUID.2003.08.005.
- Beygi, M. R., Delshad, M., Pudugramam, V. S. et al. 2015. Novel Three-Phase Compositional Relative Permeability and Three-Phase Hysteresis Models. SPE J. 20 (1): 21–34. SPE-165324-PA. https://doi.org/10.2118/165324-PA.
- Bhargava, V., Fateen, S. E. K., and Bonilla-Petriciolet, A. 2013. Cuckoo Search: A New Nature-Inspired Optimization Method for Phase Equilibrium Calculations. *Fluid Phase Equilib* 337 (6): 191–200. https://doi.org/10.1016/J.FLUID.2012.09.018.

- Bonilla-Petriciolet, A. and Segovia-Hernández, J. G. 2010. A Comparative Study of Particle Swarm Optimization and Its Variants for Phase Stability and Equilibrium Calculations in Multicomponent Reactive and Non-Reactive Systems. *Fluid Phase Equilib* 289 (2): 110–121. https://doi.org/ 10.1016/J.FLUID.2009.11.008.
- Bromley, L. A. 1973. Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions. AIChE J. 19 (2): 313–320. https://doi.org/10.1002/aic.690190216.
- Carman, P. C. 1956. Flow of Gases through Porous Media, first edition. New York, New York, USA: Academic Press.
- Cheung, A., Adjiman, C. S., Kolar, P. et al. 2002. Global Optimization for Clusters of Flexible Molecules—Solvent-Solute Interaction Energy Calculations. *Fluid Phase Equilib* 194–197: 169–183. https://doi.org/10.1016/S0378-3812(01)00780-4.
- Computer Modelling Group (CMG). 2010. CMG Software Solutions, https://www.cmgl.ca/stars.
- Davies, J. P. and Davies, D. K. 1999. Stress-Dependent Permeability: Characterization and Modeling. Paper presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, USA, 3–6 October. SPE-56813-MS. https://doi.org/10.2118/56813-MS.
- Delshad, M. and Pope, G. 1989. Comparison of the Three-Phase Oil Relative Permeability Models. *Transp Porous Media* 4 (1): 59–83. https://doi.org/ 10.1007/BF00134742.
- Di, Y., Zhang, Y., and Yu-Shu, W. 2015. Phase Equilibrium Calculation of CO₂-Hydrocarbons-Water System Based on Gibbs Free Energy Minimization (in Chinese). Acta Petrol Sin 36 (5): 593–599. https://doi.org/10.7623/syxb201505008.
- Eslami, M., Hetnarski, R., Ignaczak, J. et al. 2013. *Theory of Elasticity and Thermal Stresses*, first edition. New York, New York, USA: Solid Mechanics and Its Applications Series, Springer.
- Firoozabadi, A. and Pan, H. 2000. Fast and Robust Algorithm for Compositional Modeling: Part I—Stability Analysis Testing. Paper presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas, USA, 1–4 October. SPE-63083-MS. https://doi.org/10.2118/63083-MS.
- Grigg, R. B. and Schechter, D. S. 1997. State of the Industry in CO₂ Floods. Paper presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, 5–8 October. SPE-38849-MS. https://doi.org/10.2118/38849-MS.
- Helgeson, H. C. and Kirkham, D. H. 1974. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures: I, Summary of the Thermodynamic/Electrostatic Properties of the Solvent. American Journal Science 274 (10): 1089–1198.
- Hoffman, E. J. 1968. Flash Calculations for Petroleum Fractions. Chem Eng Sci 23 (9): 957-964. https://doi.org/10.1016/0009-2509(68)87081-2.
- Jager, M. D., Ballard, A. L., and Sloan, E. D. Jr. 2003. The Next Generation of Hydrate Prediction: II. Dedicated Aqueous Phase Fugacity Model for Hydrate Prediction. *Fluid Phase Equilib* 211 (1): 85–107. https://doi.org/10.1016/S0378-3812(03)00155-9.
- Kaya, E., Zarrouk, S. J., and O'Sullivan, M. J. 2011. Reinjection in Geothermal Fields: A Review of Worldwide Experience. *Renew. Sust. Energ. Rev.* 15 (1): 47–68. https://doi.org/10.1016/j.rser.2010.07.032.
- Kim, J., Sonnenthal, E. L., and Rutqvist, J. 2012. Formulation and Sequential Numerical Algorithms of Coupled Fluid/Heat Flow and Geomechanics for Multiple Porosity Materials. Int J Numer Methods Eng 92 (5): 425–456. https://doi.org/10.1002/nme.4340.
- Kruczek, B. 2014. Carman-Kozeny Equation. In *Encyclopedia of Membranes*, first edition, ed. E. Drioli and L. Giorno, Chap. **3**, 11–17. Berlin, Germany: Springer.
- Leibovici, C. F. and Neoschil, J. 1992. A New Look at the Rachford-Rice Equation. *Fluid Phase Equilib* 74 (4): 303–308. https://doi.org/10.1016/0378-3812(92)85069-K.
- Leibovici, C. F. and Neoschil, J. 1995. A Solution of Rachford-Rice Equations for Multiphase Systems. *Fluid Phase Equilib* **112** (2): 217–221. https://doi.org/10.1016/0378-3812(95)02797-I.
- Lemmon, W. E. 2002. NIST Reference Fluid Thermodynamic and Transport Properties—REFPROP, Version 7.0. NIST Standard Reference Database, https://ci.nii.ac.jp/naid/10021114468 (accessed 21 December 2020).
- Leverett, M. C. 1941. Capillary Behavior in Porous Solids. In *Transactions of the Society of Petroleum Engineers*, Vol. 142, Part 1, 152–169, SPE-941152-G. Richardson, Texas, USA: Society of Petroleum Engineers.
- Li, S., Li, X., and Zhang, D. 2016. A Fully Coupled Thermo-Hydro-Mechanical, Three-Dimensional Model for Hydraulic Stimulation Treatments. J Nat Gas Sci Eng 34 (August): 64–84. https://doi.org/10.1016/J.JNGSE.2016.06.046.
- Mandel, J. 1953. Consolidation Des Sols (Étude Mathématique). Géotechnique 3 (7): 287–299. https://doi.org/10.1680/geot.1953.3.7.287.
- Manrique, E. J., Thomas, C. P., Ravikiran, R. et al. 2010. EOR: Current Status and Opportunities. Paper presented at SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, 24–28 April. SPE-130113-MS. https://doi.org/10.2118/130113-MS.
- McMillan, M., Will, R., Ampomah, W. et al. 2019. Coupled Hydrodynamic-Geomechanical Modelling of CO₂-WAG Field Development at Farnsworth Unit: A Case Study. Paper presented at SPE Europec featured at the 81st EAGE Conference and Exhibition, London, UK, 3–6 June. SPE-195484-MS. https://doi.org/10.2118/195484-MS.
- McTigue, D. F. 1986. Thermoelastic Response of Fluid-Saturated Porous Rock. J Geophys Res 91 (B9): 9533–9545. https://doi.org/10.1029/ JB091iB09p09533.
- Michelsen, M. L. 1982a. The Isothermal Flash Problem: Part I Stability. Fluid Phase Equilib 9 (1): 1-19. https://doi.org/10.1016/0378-3812(82)85001-2.
- Michelsen, M. L. 1982b. The Isothermal Flash Problem. Part II. Phase-Split Calculation. Fluid Phase Equilib 9 (1): 21–40. https://doi.org/10.1016/0378-3812(82)85002-4.
- Moortgat, J., Li, Z., and Firoozabadi, A. 2012. Three-Phase Compositional Modeling of CO₂ Injection by Higher-Order Finite Element Methods with CPA Equation of State for Aqueous Phase. *Water Resour Res* **48** (12): 23–32. https://doi.org/10.1029/2011WR011736.
- Narasimhan, T. N. and Witherspoon, P. A. 1976. An Integrated Finite Difference Method for Analyzing Fluid Flow in Porous Media. Water Resour Res 12 (1): 57–64. https://doi.org/10.1029/WR012i001p00057.
- Nichita, D. V., Gomez, S., and Luna, E. 2002. Multiphase Equilibria Calculation by Direct Minimization of Gibbs Free Energy with a Global Optimization Method. *Comput Chem Eng* 26 (12): 1703–1724. https://doi.org/10.1016/S0098-1354(02)00144-8.
- Norris, A. 1992. On the Correspondence between Poroelasticity and Thermoelasticity. *J Appl Phys* **71** (3): 1138–1154. https://doi.org/10.1063/1.351278. Nowacki, W. 2013. *Thermoelasticity*, second edition. Elmsford, New York, USA: Pergamon Press.
- Okuno, R., Johns, R., and Sepehrnoori, K. 2010a. A New Algorithm for Rachford-Rice for Multiphase Compositional Simulation. SPE J. 15 (2): 313–325. SPE-117752-PA. https://doi.org/10.2118/117752-PA.
- Okuno, R., Johns, R. T., and Sepehrnoori, K. 2010b. Three-Phase Flash in Compositional Simulation Using a Reduced Method. SPE J. 15 (3): 689–703. SPE-125226-PA. https://doi.org/10.2118/125226-PA.
- Pan, L. and Oldenburg, C. M. 2016. TOGA: A TOUGH Code for Modeling Three-Phase, Multi-Component, and Non-Isothermal Processes Involved in CO₂-Based Enhanced Oil Recovery. Technical Report LBNL-1006472, Lawrence Berkeley National Laboratory, Berkeley, California, USA (October 2016).
- Park, H. 2019. Polytope Bounded Voronoi Diagram in 2D and 3D, Github, https://www.github.com/hyongju/Polytope-bounded-Voronoi-diagram (accessed 27 October 2020).
- Prakash, R., Kana Nguene, P., Seers, T. D. et al. 2019. Chemo-Mechanical Investigation of CO₂-Fluid-Rock Interaction in CO₂ Storage and CO₂-EOR Processes in Unconventional Reservoirs. Paper presented at the 53rd US Rock Mechanics/Geomechanics Symposium, New York, New York, USA, 23–26 June. ARMA-2019-1983.

- Pruess, K. and Bodvarsson, G. S. 1984. Thermal Effects of Reinjection in Geothermal Reservoirs with Major Vertical Fractures. *J Pet Technol* **36** (9): 1567–1578. SPE-12099-PA. https://doi.org/10.2118/12099-PA.
- Rao, D. 2001. Gas Injection EOR—A New Meaning in the New Millennium. J Can Pet Technol 40 (2): 12–45. PETSOC-01-02-DAS. https://doi.org/ 10.2118/01-02-DAS.
- Reem, D. 2009. An Algorithm for Computing Voronoi Diagrams of General Generators in General Normed Spaces. Proc., 2009 Sixth International Symposium on Voronoi Diagrams, Copenhagen, Denmark, 23–26 June, 144–152. https://doi.org/10.1109/ISVD.2009.23.
- Rezaveisi, M., Sepehrnoori, K., Pope, G. A. et al. 2018. Thermodynamic Analysis of Phase Behavior at High Capillary Pressure. SPE J. 23 (6): 1977–1990. SPE-175135-PA. https://doi.org/10.2118/175135-PA.
- Rossi, C. C. R. S., Cardozo-Filho, L., and Guirardello, R. 2009. Gibbs Free Energy Minimization for the Calculation of Chemical and Phase Equilibrium Using Linear Programming. *Fluid Phase Equilib* 278 (1–2): 117–128. https://doi.org/10.1016/J.FLUID.2009.01.007.
- Rutqvist, J. 1995. Determination of Hydraulic Normal Stiffness of Fractures in Hard Rock from Well Testing. *Int J Rock Mech Min Sci* **32** (5): 513–523. https://doi.org/10.1016/0148-9062(95)00039-J.
- Rutqvist, J., Freifeld, B., Min, K.-B. et al. 2008. Analysis of Thermally Induced Changes in Fractured Rock Permeability during 8 Years of Heating and Cooling at the Yucca Mountain Drift Scale Test. *Int J Rock Mech Min Sci* **45** (8): 1373–1389. https://doi.org/10.1016/j.ijrmms.2008.01.016.
- Rutqvist, J., Wu, Y.-S., Tsang, C.-F. et al. 2002. A Modeling Approach for Analysis of Coupled Multiphase Fluid Flow, Heat Transfer, and Deformation in Fractured Porous Rock. *Int J Rock Mech Min Sci* **39** (4): 429–442. https://doi.org/10.1016/S1365-1609(02)00022-9.
- Salimzadeh, S., Paluszny, A., and Zimmerman, R. W. 2018. Effect of Cold CO₂ Injection on Fracture Apertures and Growth. *Int. J. Greenh. Gas Control* **74** (July): 130–141. https://doi.org/10.1016/j.ijggc.2018.04.013.
- Schlumberger. 2009. INTERSECTSM High-Resolution Reservoir Simulator. https://www.software.slb.com/products/intersect.
- Shock, E. L. and Helgeson, H. C. 1988. Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Correlation Algorithms for Ionic Species and Equation of State Predictions to 5 Kb and 1000°C. *Geochim Cosmochim Acta* 52 (8): 2009–2036. https://doi.org/10.1016/0016-7037(88)90181-0.
- Stefansson, V-D. 1997. Geothermal Reinjection Experience. Geothermics 26 (1): 99–139. https://doi.org/10.1016/S0375-6505(96)00035-1.
- Tang, H., Wang, S., Yin, C. et al. 2019. Fully-Coupled Multi-Physical Simulation with Physics-Based Nonlinearity-Elimination Preconditioned Inexact Newton Method for Enhanced Oil Recovery. *Commun Comput Phys* 25 (1): 244–265. https://doi.org/10.4208/cicp.OA-2017-0108.
- Taron, J., Elsworth, D., and Min, K.-B. 2009. Numerical Simulation of Thermal-Hydrologic-Mechanical-Chemical Processes in Deformable, Fractured Porous Media. Int J Rock Mech Min Sci 46 (5): 842–854. https://doi.org/10.1016/j.ijrmms.2009.01.008.
- Walton, S., Hassan, O., Morgan, K. et al. 2011. Modified Cuckoo Search: A New Gradient Free Optimisation Algorithm. *Chaos Solitons Fractals* 44 (9): 710–718. https://doi.org/10.1016/J.CHAOS.2011.06.004.
- Wang, L., Tian, Y., Yu, X. et al. 2017a. Advances in Improved/Enhanced Oil Recovery Technologies for Tight and Shale Reservoirs. *Fuel* **210** (2): 425–445. https://doi.org/10.1016/J.FUEL.2017.08.095.
- Wang, L., Wang, S., Zhang, R. et al. 2017b. Review of Multi-Scale and Multi-Physical Simulation Technologies for Shale and Tight Gas Reservoirs. J Nat Gas Sci Eng 37 (3): 560–578. https://doi.org/10.1016/j.jngse.2016.11.051.
- Wang, S. 2015. Numerical Study of Thermal-Hydraulic-Mechanical Behavior of Fractured Geothermal Reservoirs. PhD dissertation, Colorado School of Mines, Golden, Colorado.
- Wang, S., Huang, Z., Wu, Y.-S. et al. 2016. A Semi-Analytical Correlation of Thermal-Hydraulic-Mechanical Behavior of Fractures and Its Application to Modeling Reservoir Scale Cold Water Injection Problems in Enhanced Geothermal Reservoirs. *Geothermics* 64 (1): 81–95. https://doi.org/ 10.1016/j.geothermics.2016.04.005.
- Wang, S., Lukyanov, A. A., and Wu, Y.-S. 2019a. Second-Order Gas Slippage Model for the Klinkenberg Effect of Multicomponent Gas at Finite Knudsen Numbers Up To 1. Fuel 235 (1 January): 1275–1286. https://doi.org/10.1016/J.FUEL.2018.08.113.
- Wang, S., Lukyanov, A. A., and Wu, Y.-S. 2019b. Application of Algebraic Smoothing Aggregation Two Level Preconditioner to Multiphysics Fluid Flow Simulations in Porous Media. Paper presented at the SPE Reservoir Simulation Conference, Galveston, Texas, USA, 10–11 April. SPE-193870-MS. https://doi.org/10.2118/193870-MS.
- Wilson, G. M. 1964. Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. J. Am. Chem. Soc. 86 (2): 127–130. https://doi.org/10.1021/ja01056a002.
- Yang, T., Fevang, O., Christoffersen, K. R. et al. 2007. LBC Viscosity Modeling of Gas Condensate to Heavy Oil. Paper presented at SPE Annual Technical Conference and Exhibition, Anaheim, California, USA, 11–14 November. SPE-109892-MS. https://doi.org/10.2118/109892-MS.
- Yang, Y., Li, Y., Yao, J. et al. 2020. Dynamic Pore-Scale Dissolution by CO₂-Saturated Brine in Carbonates: Impact of Homogeneous versus Fractured versus Vuggy Pore Structure. *Water Resour Res* 56 (4). https://doi.org/10.1029/2019WR026112.
- Yarborough, L. 1972. Vapor-Liquid Equilibrium Data for Multicomponent Mixtures Containing Hydrocarbon and Nonhydrocarbon Components. J. Chem. Eng. Data 17 (2): 129–133. https://doi.org/10.1021/je60053a027.
- Yuan, C. and Pope, G. A. 2011. A New Method To Model Relative Permeability in Compositional Simulators To Avoid Discontinuous Changes Caused by Phase Identification Problems. Paper presented at the SPE Reservoir Simulation Symposium, The Woodlands, Texas, USA, 21–23 February. SPE-142093-MS. https://doi.org/10.2118/142093-MS.
- Zhang, H., Bonilla-Petriciolet, A., and Rangaiah, G. P. 2011. A Review on Global Optimization Methods for Phase Equilibrium Modeling and Calculations. Open Thermodyn. J. 5 (1): 71–92. https://doi.org/10.2174/1874396X01105010071.
- Zhang, N., Wei, M., and Bai, B. 2018. Comprehensive Review of Worldwide CO₂ Immiscible Flooding. Paper presented at the SPE Improved Oil Recovery Conference, Tulsa, Oklahoma, USA, 14–18 April. SPE-190158-MS. https://doi.org/10.2118/190158-MS.
- Zhang, Y., Lashgari, H. R., Di, Y. et al. 2016. Capillary Pressure Effect on Hydrocarbon Phase Behavior in Unconventional Reservoirs. Paper presented at the SPE Low Perm Symposium, Denver, Colorado, USA, 5–6 May. SPE-180235-MS. https://doi.org/10.2118/180235-MS.
- Zhu, Z., Fang, C., Qiao, R. et al. 2020. Experimental and Molecular Insights on Mitigation of Hydrocarbon Sieving in Niobrara Shale by CO₂ Huff 'N'Puff. SPE J. 25 (4): 1803–1811. SPE-196136-PA. https://doi.org/10.2118/196136-PA.

Appendix A—Equation of State and Fugacity Model

The calculation of the Gibbs free energy requires the calculation of the fugacity of the component, which is achieved by the reformulation of an equation of state. In MSFLOW_CO2, the Soave-Redlich-Kwong equation of state is used for the calculation of the density as well as the fugacity of the vapor-hydrocarbon and the liquid-hydrocarbon phases. The fugacity of the vapor-hydrocarbon and the liquid-hydrocarbon phases is shown by

where Z is the compressibility factor and x_j and y_j are the mole fractions, as defined previously. In Eqs. A-1 and A-2, the parameter a is defined as

$$a = \sum_{i=1}^{N_C} \sum_{j=1}^{N_C} x_i x_j a_{ij}. \qquad (A-3)$$

 a_{ij} is defined as

where k_{ij} is the interaction parameter, listed in Appendix C.

 a_i and α_i are defined as

$$a_i = 0.42747 \frac{R^2 T_{CR_i}^2}{P_{CR_i}}, \qquad (A-5)$$

where T_{CR_i} and P_{CR_i} are the critical temperature and critical pressure of component *i*, respectively,

$$\alpha_i = \left[1 + S_i^* \left(1 - \sqrt{T_{r_i}}\right)\right]^2, \quad \dots \quad (A-6)$$

where

 $S_i^* = 0.48508 + 1.55151\omega_i - 0.15613\omega_i^2. \quad (A-7)$

The reduced temperature and pressure are defined as

$$T_{r_i} = \frac{T}{T_{CR_i}}, \qquad (A-8)$$

$$P_{r_i} = \frac{P}{P_{CR_i}}, \qquad (A-9)$$

where ω_i is the acentric parameter of component *i*,

$$b = \sum_{i=1}^{N_{C}} x_{i}b_{i}, \qquad \dots \qquad (A-10)$$

$$b_{i} = 0.08664 \frac{RT_{CR_{i}}}{P_{CR_{i}}}. \qquad (A-11)$$

The aqueous (water)-phase properties are calculated using the Shock and Helgeson (1988) approach. The chemical potential μ_{iAq} of the *i*th solute component (nonwater component) in the water phase is calculated as

where T_0 and P_0 are the standard temperature and pressure, respectively, and \overline{g}_i^* , \overline{h}_i^* , and \overline{v}_i^* are the partial molar Gibbs energy, partial molar enthalpy, and partial molar volume of a hypothetical solution, respectively. The detailed formulations of \overline{g}_i^* , \overline{h}_i^* , and \overline{v}_i^* can be found in Shock and Helgeson (1988). The chemical potential of the water component in the water phase is calculated as

where the subscript "pure" refers to the pure-water phase. The details of the implementation of water fugacity can be found in Bromley (1973) and Jager et al. (2003).

Appendix B—Thermal, Hydraulic, and Rock Mechanical Properties

 h_{β} , the enthalpy of the hydrocarbon phase β , is calculated using a simple mixing rule based on the enthalpy of the pure components,

$$h_{\beta} = \sum_{i=1}^{N_C} x_{i\beta} h_i, \quad \beta = G, L, \quad \dots \quad (B-1)$$

where h_i is retrieved from Lemmon (2002). We use a linear function of temperature to regress the data,

$$h_i = a_0 + a_1(T - 275)$$
. (B-2)

The critical temperature (T_c), critical pressure (P_c), acentric factor (w), molecular weight, and two enthalpy parameters (a_0, a_1) are listed in Appendix C. The enthalpy of the water phase is directly from the TOUGH2 simulator, as used by Wang et al. (2016).

The mechanical properties have effects on the permeability as well as the porosity of the formation rock. In general, the porosity and permeability can be expressed as a function of pressure, temperature, and mean stress, as

$\phi = \phi(P, T, \sigma_m),$	 	 	 	•••••	(B-3)
$K = K(P, T, \sigma_m).$	 	 	 		(B-4)

MSFLOW_CO2 has implemented several correlations for permeability and porosity from the literature (Rutqvist et al. 2002; Taron et al. 2009; Wang et al. 2016). Moreover, MSFLOW_CO2 allows the user to enter a table of permeability and porosity with respect to the primary variables. One example of these correlations is as follows (Wang et al. 2017a, 2017b). The porosity of the rock can be calculated as

$$\phi = \phi_0 [1 + c_p (P - P_{\text{ref}}) + 3\beta_T (T - T_{\text{ref}})], \quad \dots \quad (B-5)$$

where c_p and β_T are the compressibility and the thermal-expansion coefficient, respectively; P_{ref} is a reference pressure and T_{ref} is a reference temperature; and ϕ_0 and ϕ are the initial porosity and the transient porosity of the rock, respectively. Another correlation directly correlates the porosity with the effective mean stress (Davies and Davies 1999; Rutqvist et al. 2002),

where ϕ_r is the residual porosity at maximum stress, ϕ_0 is the porosity when the stress is zero, and σ'_m is the mean effective stress. The change of the mean effective stress is calculated by

where β is the linear thermal-expansion coefficient and K_B is the bulk modulus.

Using the calculated porosity, the permeability can be calculated from the Carman-Kozeny equation (Carman 1956; Kruczek 2014) as

$$K = K_0 \left(\frac{1-\phi_0}{1-\phi}\right)^3 \left(\frac{\phi}{\phi_0}\right)^3. \tag{B-8}$$

Moreover, the mechanical effect on the gridblock volume is quantified by means of the volumetric strain ε_V as

where V_0 and V are the initial and the transient volume of the gridblock, respectively.

In MSFLOW_CO2, the three-phase relative permeability is calculated using the extended Brooks-Corey model (Delshad and Pope 1989),

$$k_{ro} = k_{ro,max} \left(\frac{S_o - S_{or}}{1 - S_{or} - S_{wr} - S_{gr}} \right)^{n_o}, \qquad (B-10)$$

$$k_{rw} = k_{rw,max} \left(\frac{S_w - S_{wr}}{1 - S_{or} - S_{wr} - S_{gr}} \right)^{n_w}, \qquad (B-11)$$

$$k_{rg} = k_{rg,max} \left(\frac{S_g - S_{gr}}{1 - S_{or} - S_{wr} - S_{gr}} \right)^{n_g}, \qquad (B-12)$$

where $k_{ro,max}$, $k_{rw,max}$, and $k_{rg,max}$ are the maximum relative permeability for the liquid-hydrocarbon phase, the aqueous phase, and the gas phase, respectively, while S_{or} , S_{wr} , and S_{gr} are the residual relative permeability for each phase, respectively. By default, n_o , n_w , and n_w are set to 3.0, 2.0, and 3.0 for water-wet reservoirs.

The viscosities of the hydrocarbon phases are calculated from the classical Lohrenz-Bray-Clark viscosity correlation, in which the parameters are taken from the work of Yang et al. (2007). The viscosity of the aqueous phase with dissolved CO_2 is calculated using the correlation adopted in Pan and Oldenburg (2016). Because the correlations are very lengthy, we do not list the detailed formulations in this manuscript. Interested readers can refer to the Yang et al. (2007) and Pan and Oldenburg (2016).

Appendix C—Parameters for Flash Calculation

 Table C-1 lists the binary-interaction coefficients for the calculation of pressure/volume/temperature properties.
 Table C-2 lists the critical properties, acentric factor, molecular weights, enthalpy parameters, and parachor of each of the components used in this study.

	CH_4	C_2H_6	C_3H_8	<i>n</i> -C ₄ H ₁₀	<i>n</i> -C ₅ H ₁₂	<i>n</i> -C ₆ H ₁₄	<i>n</i> -C ₇ H ₁₆	<i>п</i> -С ₈ Н ₁₈	<i>n</i> -C ₉ H ₂₀	<i>n</i> -C ₁₀ H ₂₂	CO_2	H ₂ O	
CH_4	0	0	0.01	0.01	0.02	0.04	0.04	0.05	0.05	0.05	0	0	
C_2H_6	0	0	0	0.01	0.01	0.01	0.02	0.02	0.02	0.03	0	0	
C_3H_8	0.01	0	0	0	0.01	0.03	0.06	0.06	0.01	0.02	0	0	
<i>n</i> -C ₄ H ₁₀	0.01	0.01	0	0	0.02	0.02	0.02	0.01	0.01	0	0	0	
<i>n</i> -C ₅ H ₁₂	0.02	0.01	0.01	0.02	0	0	0	0	0	0	0	0	
<i>n</i> -C ₆ H ₁₄	0.04	0.01	0.03	0.02	0	0	0	0	0	0	0	0	
<i>n</i> -C ₇ H ₁₆	0.04	0.02	0.06	0.02	0	0	0	0	0	0	0	0	
<i>n</i> -C ₈ H ₁₈	0.05	0.02	0.06	0.01	0	0	0	0	0	0	0	0	
<i>n</i> -C ₉ H ₂₀	0.05	0.02	0.01	0.01	0	0	0	0	0	0	0	0	
<i>n</i> -C ₁₀ H ₂₂	0.05	0.03	0.02	0	0	0	0	0	0	0	0	0	
CO ₂	0	0	0	0	0	0	0	0	0	0	0	0	
H ₂ O	0	0	0	0	0	0	0	0	0	0	0	0	

Table C-1—Binary-interaction coefficients for the calculation of properties.

	<i>T_c</i> (K)	P_c (MPa)	W	MW (g⋅mol ⁻¹)	<i>a</i> ₀ [KJ·(kg·K) ⁻¹]	$a_1 [\text{KJ} \cdot (\text{kg} \cdot \text{K})^{-1}]$	Parachor
CH ₄	190.56	4.599	0.0115	16.043	2.191	0.002672	77.0
C_2H_6	305.32	4.872	0.0995	30.07	1.651	0.004384	108.0
C ₃ H ₈	369.83	4.248	0.1523	44.096	0.79	0.00468	150.3
<i>n</i> -C ₄ H ₁₀	408.14	3.648	0.2002	58.123	0.818	0.004255	203.4
<i>n</i> -C ₅ H ₁₂	469.7	3.37	0.2515	72.15	-0.218	0.001895	231.5
<i>n</i> -C ₆ H ₁₄	507.6	3.025	0.3013	86.177	-0.491	0.007187	271.0
<i>n</i> -C ₇ H ₁₆	540.2	2.74	0.3495	100.204	-0.756	0.007811	312.5
<i>n</i> -C ₈ H ₁₈	568.7	2.49	0.3996	114.231	-0.989	0.00836	351.5
<i>n</i> -C ₉ H ₂₀	594.6	2.29	0.4435	128.258	-1.236	0.008951	393.0
<i>n</i> -C ₁₀ H ₂₂	617.7	2.11	0.4923	142.285	-1.465	0.009484	617.7
CO ₂	304.3	7.39	0.2236	44.01	0.727	0.003722	446.2
H ₂ O	647.3	22.06	0.3440	18.015	-	-	110.0
H ₂ S	373.5	9.01	0.2704	34.01	0.402	0.00283	80.1

Table C-2—Parameters for the calculation of component properties. MW = molecular weight.