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A General Purpose Reservoir Simulation Framework for Multiphase Multicomponent Reactive Fluids

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Abstract

Reservoir simulation models describe the flow of various fluid models, such as black oil, compositional, reactive transport, and chemical flooding. Implementing new fluid models in reservoir simulators requires significant manpower to rewrite the simulation code, especially if the original simulator was not designed properly. One such example is to include geochemical reactive transport processes. In this paper, a general modeling framework is developed for easy implementation of new fluid models including time-independent (equilibrium) and time-dependent (kinetic) correlations. The approach is physically sound, robust and naturally extends black oil and compositional models to multiphase reactive systems for a variety of complex flow processes.

The fundamental physical laws (including conservation laws of mass/momentum/energy and thermodynamics laws) govern multiphase flow in porous media. Here we consistently applied the general principles under different assumptions to obtain the mass conservation equations for various processes. The framework includes a definition of components under the instantaneous phase and chemical equilibrium, mass conservation equations, a volume balance equation, and equilibrium relations. That is, primary equations for various fluids are represented by a unique set of mass conservation equations with different secondary algebraic constraints. The differential equations do not need to be changed as new processes are added. IMPEC and FIM are used to solve for flow. A robust algorithm is developed to calculate the phase equilibrium together with chemical equilibrium.

The simulator was validated with SPE comparative solution projects using Eclipse 300 and CMG-GEM. Large-scale reservoir models including SPE 10 and a field case from Europe were compared with various commercial simulators, showing that the simulator is significantly faster and more robust. New coupled reactive phase behavior models were implemented, including low salinity waterflooding, CO₂ WAG with reactions, alkali/surfactant/polymer (ASP) flooding with the HLD-NAC EoS model, and fines migration. Those models have been implemented with minimal additional coding owing to the novel and consistent framework. The modeling framework provides a handy and powerful tool to understand the detailed interaction between species, easily update the physics as needed, and to better predict its impact on the ultimate oil recovery. This framework differs from previous research because the equilibrium chemical reactions are included without changing the structure of the compositional model. Similar to conventional compositional models, the flow, transport and local interactions are treated in two parts. This

paper generalizes the simulation technology (named PennSim) that we have used in various applications. The novel formulation also enables fast linear solver performance due to the natural decoupling techniques.

Introduction

Modeling of multiphase flow in porous media is of fundamental importance to petroleum and environmental engineering. Mathematical models describe and predict the flow and transport of hydrocarbon and aqueous fluids, which greatly improve reservoir management. Flow and transport behavior is complex since the crude oil and underground brine contain numerous components and multiple phases, including aqueous, oleic, and vapor phases. Other phases such as microemulsions and secondary liquid phases can also exist depending on the processes. Processes are typically coupled, including mass transfer between phases, adsorption/desorption and chemical reactions. Those complexities prohibit a simple representation of the fluid system with many variables and equations that form a challenging nonlinear system of equations.

There has been a considerable effort in the development of robust and efficient oil reservoir simulators over the last several decades that describe various processes. The black oil and compositional models are two of the most popular models for reservoir simulation. The black oil model is the most widely used reservoir simulation model because of the easy-setup, low-computational-cost and robustness. Most popular black oil simulators, such as Eclipse (Eclipse 2009), CMG-IMEX (CMG 2012), SENSOR (Coats et al. 1998) use pressure and saturation as the primary unknowns.

Equations of state (EOS) can accurately model the pressure, volume and temperature (PVT) properties of hydrocarbon fluids. In EOS compositional models, the partitioning of components into phases is determined by thermodynamic equilibrium represented by fugacity. The unknown phase molar fractions, phase saturations, and pressures are correlated through implicit local equations (fugacity equations). The phases must be labeled so that their saturation can be used for relative permeability calculation. The phase labeling can be practically impossible for miscible floods and the discontinuity in phase labeling can make compositional simulators less robust (Yuan and Pope 2012). Since there are many unknowns, the early work on compositional models focused on the choice of primary unknowns so that the total number of unknowns is reduced. Primary unknowns are solved first from primary equations, and secondary unknowns are calculated from the primary unknowns. The choices of primary variable sets are classified into two categories, natural variables and mass variables. The natural variable set was first proposed by Coats (1980), where the primary variables are P , x_{ig} ($i = 3, \dots, n_c$) and S_j ($j = o, w$). The mass conservation equations are chosen as the primary equations. Other constraint equations are used to eliminate the secondary variables from the primary equations. Besides the 1980 model, simulators that use the natural set of primary unknowns include Quandalle and Savary 1989, Branco and Rodriguez 1996, Coats et al. 1998, Cao 2002.

The mass variable set uses the overall molar density or the overall molar composition as the primary unknowns. While the accumulation term is linear, the volume constraint equation or the saturation equation becomes highly nonlinear. Out of the numerous mass variable sets used in simulators (e.g. Wong et al. 1987, Young and Stephenson 1983, Chien 1985, Nghiem et al. 1981), one representative type uses P and N_i as primary unknowns (Acs et al. 1985; Chang 1990; Collins et al. 1992; Watts 1986). The mass conservation and volume balance equations are typically chosen in these simulators as the primary equations. For all of these mass-variable methods, a phase stability test is performed at each iteration to determine if the mixture will split into two phases. Flash calculations are performed to obtain the phase molar fractions if two phases form. One major advantage of mass variable sets over the natural variable set is that when the phase state changes (phase appearance and disappearance) the primary variables do not need to be change.

Sequential schemes can be derived taking advantage of the weak coupling between the mass conservation equations and fugacity equations for small time-step sizes. The Implicit Pressure Explicit Composition (IMPEC) methods for EOS compositional models can be derived in several ways, such as by Gaussian elimination of the Jacobian matrix and the volume-balance method (Wong et al. 1987). Wong et al. (1990)

proved that the Gaussian elimination approach and the volume balance approach lead to the same Jacobian matrix for the pressure solution. However, the Gaussian elimination method requires the formulation of a global Jacobian matrix first. For the fully implicit method (FIM), different primary variables have been used and the performance compared for an EOS compositional model (Voskov et al. 2009). All methods tested in their paper converged similarly when the time-step size was small. When the time-step size was large, the natural variable sets had an advantage over others. Other methods such as IMPSAT (Cao 2002; Quandalle and Savary 1989) and AIM (Collins et al. 1992) tend to reduce the size of the full Jacobian matrix, which in turn reduces the workload of the linear solver.

Reactive transport models have been applied extensively to understand chemical and biological processes in earth systems (Lichtner 1996; Steefel and Lasaga 1994). For fast reactions, local equilibrium is assumed, which introduces a set of nonlinear algebraic equations. For slow reactions, reaction kinetic laws give an expression of reaction rates. Geochemical simulators are developed to model problems like CO₂ sequestration, nuclear contamination, and other applications (Li et al. 2009). So far the application of those geochemical simulators (or reactive transport simulators) is mostly in environmental engineering while the effort to couple more processes continues (e.g., Fan et al. 2012). It is desirable to add the chemical reactions or any novel fluid models to a mature reservoir simulation code such that the reaction-coupled processes can be simulated without re-developing a complete new set of codes.

In many applications, both phase equilibrium and chemical reactions are important. In such cases, the reactants and products of the reactions could be transferred between phases. Coupled with reactive transport modeling, compositional modeling can provide an integrative approach to understand the complex processes. A few existing simulators in the literature can model oil and gas equilibrium coupled with geochemical reactions (Delshad et al. 2011; Fan et al. 2012; Nghiem et al. 2011; Wei 2012). In addition, the simulation of chemical enhanced oil recovery also requires special phase behavior and fluid property models.

Several recent methods for including chemical reactions also have limitations in their applicability. Wei (2012) modeled the system using a sequential method, where phase equilibrium was first solved followed by chemical reactions. This method cannot maintain equilibrium between systems. Delshad et al. (2011) solved the system in a similar way while the solution steps were iterated until convergence was reached. Fan et al. (2012) proposed an element-based method, but in this approach, the full Jacobian matrix needs to be constructed before the transformation matrix is multiplied.

It is common to use different simulators (codes) for different types of processes or fluid type. For example, UTCHEM is well known for chemical floods while UTCOMP is known for gas flooding. Whenever new features (such as new visualization API or advanced meshing) are added, they are applied only for a specific code, thereby requiring more effort if all codes would be updated similarly. Our goal is to develop a reusable code that is extensible in fluid types while sharing other features, such as having an unstructured grid, IMPEC or FIM flow solution and linear solvers. That is, we define a set of unique notations and equations such that those equations hold for various fluid models. Unlike the different formulations of compositional models that are mostly concerned with speed, we focus on the generality and use a set of consistent notations that can be reused for different applications.

Methodology

In this section, we describe a framework to organize reservoir fluid and flow models. The purpose of the framework is to manage the code development and testing for novel complex fluid models in a timely manner. We first revisit the fundamental concepts and then list the general flow equations. Next we discuss the existing fluid models and specify what a component represents for different fluid models. We are not proposing new numerical schemes. Instead, we are proposing an improved way of organizing modules for complex flow processes in reservoir engineering.

Component concepts based on species.

An accurate description of multiphase flow in porous media in oil fields requires equal knowledge of petrophysics, geochemistry and mathematics. Here we clarify three important concepts before we move forward.

A phase is a region of space (a thermodynamic system) throughout which all physical properties of a material are essentially uniform (Tester and Modell 1997). In other words, a phase is one distinctive substance that has homogeneous properties such as density, viscosity and fluid velocity. Different phases have clear boundaries between each other. Possible phases in petroleum engineering include the liquid phase (l), the aqueous phase (aq), the vapor phase (v), the solid phase (s), the CO₂ rich secondary liquid phase (l₂) and the microemulsion phase (m).

A species (or chemical species) is an ensemble of chemically identical molecular entities that have the same set of molecular energy levels on the time scale of interest (Iupac 2009). The concept of species in compositional models is a chemical entity, which is distinguishable by its molecular formula and the phase in which it exists (Nghiem et al. 2011). For example, H₂O(aq) is one species, representing the water molecule in the aqueous phase, while H₂O(v) is another species, representing the water molecule in the vapor phase. Other examples of species are the bicarbonate ion in the aqueous phase HCO₃⁻(aq), methane in the vapor phase CH₄(v), pentane in the liquid phase C₅H₁₂(l), decane in the liquid phase nC₁₀(l) and asphaltene in the solid phase. A phase is a homogeneous mixture of species.

A component (or chemical component) is a chemically-independent constituent of a system. The number of components represents the minimum number of independent species necessary to define the composition of all phases of the system (Atkins and De Paula 2002). Namely, the number of components equals the degree of freedom of a given system. In a compositional model without reactions, a component is a chemical entity that is distinguishable by its molecular formula (Nghiem et al. 2011). The definition of a component in the conventional compositional models does not apply to a system with chemical reactions. A component is essentially one distinguishable set of species, the molar amount of which is conserved under instantaneous transformations. The number of components in a system equals the number of species minus the number of constraints, including thermodynamic equilibrium, chemical equilibrium and the charge neutrality condition. The definition of a component depends on the existing species and all transformations between the species. For example, the CO₂ component refers to all the CO₂ species, including CO₂(v), CO₂(aq), CO₂(l) and the possible ionic species CO₃²⁻ and HCO₃⁻; the C₆ component refers to the sum of C₆(g) and C₆(l). If one species can be transformed to another species, through mass transfer between phases or chemical reactions, the two species belong to one component. With equilibrium chemical reactions and phase transitions, the molar amount of a component refers to the conserved amount of substance under instantaneous transitions. Therefore, we need to be more careful to use the definition "component" when there is instantaneous reactions between species with different chemical formula.

In summary, a species is defined to be the substance that has the same chemical formula and resides in one phase; a component is a group of species that have a conserved mass/mole quantity that is independent of reactions or instantaneous mass transfers between phases.

General framework.

We define n_c components for each system, where component i has a total molar bulk density N_i defined as

$$N_i = \frac{\text{total mole or mass of component } i}{\text{bulk volume of porous media}}.$$

Here we can ensure that N_i does not change during instantaneous reactions and phase equilibrium by defining N_i according to each fluid system, which we will discuss in a later section. The total molar density of component i in phase i is defined as

$$\omega_{ij} = \frac{\text{total mole or mass of component } i \text{ in phase } j}{\text{volume of phase } j}.$$

There are n_p phases in the system, and the effective velocity (length/time) for each phase is \vec{u}_j , which follows from Darcy's law:

$$\vec{u}_j = -\frac{k k_{rj}}{\mu_j} \nabla(P + P_{cj} - \gamma_c \rho_j D). \quad (1)$$

Here the notation is based on the classic multiphase flow model: k denotes the permeability; k_{rj} the relative permeability for phase j ; P_{cj} the capillary pressure of phase j relative to the reference phase; ρ_j is the mass density; γ_c is the gravitational factor; and D is the depth. The molar/mass conservation equation can be written as

$$\frac{\partial}{\partial t} N_i + \nabla \cdot \left(-\sum_{j=1}^{n_p} \frac{k k_{rj}}{\mu_j} \omega_{ij} \nabla(P + P_{cj} - \gamma_c \rho_j D) \right) + Q_i + R_i = 0, \quad i = 1, \dots, n_c \quad (2)$$

where Q_i denotes the total molar/mass rate of source/sink for component i , and R_i denotes the total molar or mass rate of slow chemical reaction (not instantaneous) for component i .

In porous media, fluids always fill the pores so that the total of all phases is equal to the pore volume,

$$\phi = \sum_{j=1}^{n_p} v_j \quad (3)$$

where ϕ is a pressure-dependent porosity; v_j is the fluid volume of phase j per bulk volume. At a given temperature, pressure P and n_c total moles N_i 's, the thermodynamic state of the substance is fixed. Namely, all the fluid and rock properties for isothermal flow are functions of P and N_i 's. We define the primary unknowns $\mathbf{X}_p = (P, N_1, \dots, N_{n_c})^T$ and secondary unknowns

$$\mathbf{X}_s = (\omega_{11}, \omega_{12}, \dots, \omega_{n_c n_p}, \mu_1, \dots, \mu_{n_p}, \rho_1, \dots, \rho_{n_p}, v_1, \dots, v_{n_p}, k_{r1}, \dots, k_{rn_p}, P_{c1}, \dots, P_{cn_p}, R_1, \dots, R_{n_c})^T$$

such that the second unknowns are functions of primary unknowns written as

$$\mathbf{X}_s = \mathbb{F}(\mathbf{X}_p).$$

This function can be an explicit or implicit function depending on the fluid type, where its Jacobian matrix can also be calculated:

$$\frac{\partial \mathbf{X}_s}{\partial \mathbf{X}_p} = \mathbb{J}(\mathbf{X}_p). \quad (4)$$

Similar to a total molar formulation for the EOS compositional model (Collins et al. 1992), we use equation (1) and (2) as the $n_c + 1$ primary equations, and \mathbf{X}_p as the $N_c + 1$ primary variables. The equation system is then closed. The phase behavior/reactions can be separated to calculate the \mathbb{F} and \mathbb{J} function. The structure of the framework is shown in Figure 1. The numerical implementation can be found in Qiao (2015).

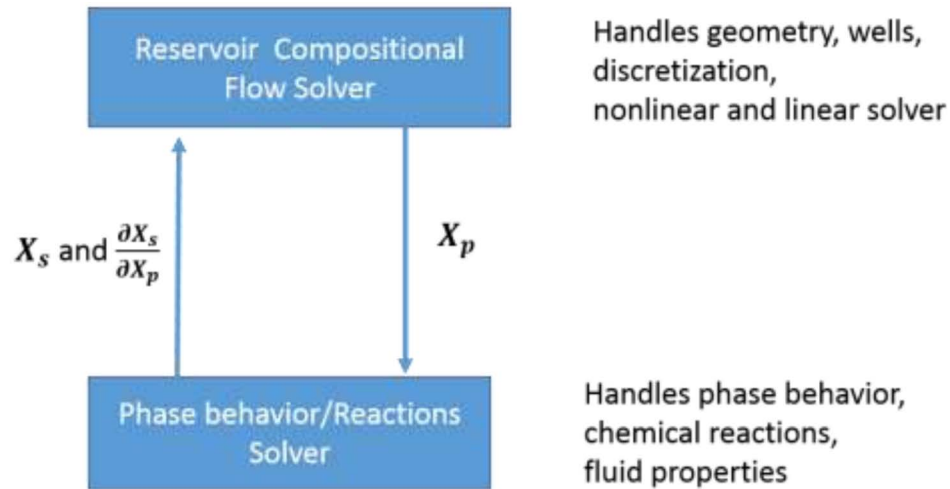


Figure 1—Schematic illustration of the general framework.

Types of fluid models.

The most widely used reservoir fluid models are the black oil and the cubic equation of state (EOS) compositional model. These models have been used in field scale simulations, and a wide variety of simulators are available (e.g., [Eclipse 2009](#) and [CMG 1995](#)). Recently, reactive transport models also have attracted more attention in petroleum fields due to their application in enhanced oil recovery, well stimulation, and processes where chemical reactions cannot be neglected. In addition, surfactant flooding phase behavior models require improvements in accuracy for field scale simulations. Those distinct fluid models can be organized in such a way that different features and properties are handled, while a general fluid flow transport part is preserved. In the following, we discuss what the components represent for each fluid type and the equilibrium conditions that form functions \mathbb{F} and \mathbb{J} .

Black oil model.

In the conventional black oil model, the oil phase is considered as a mixture of two pseudo-components, oil and gas. The pressure and the amount of gas in the oil phase (solution gas-oil ratio) determine if a vapor phase will form. Densities and viscosities are interpolated as functions of pressure and solution gas-oil ratio. The relative permeability and capillary pressure are functions of saturation. In short, black oil models consider three components (two hydrocarbon pseudo-components and the water component) in three phases (vapor, oleic and aqueous), while the properties are functions of pressure and composition. A black oil model can be written using the compositional formulation with simple PVT relations ([Nojabaei et al. 2014](#); [Wong et al. 1987](#)). The species for the black oil model are shown in [Table 1](#), where m_k denotes the moles of species k per bulk volume. [Table 2](#) gives the equilibrium condition for such systems, where the gas/oil ratio is a function of pressure when oil is saturated and phase behavior equilibrium is treated as a chemical reaction.

Table 1—Species – Components for standard black oil model.

Component	Species	Total amount of component
Oil	pseudo-oil in liquid phase (oL)	$N_1 = m_{oL}$
Gas	pseudo-gas in vapor phase(gV), pseudo-gas dissolved in liquid phase(gL)	$N_2 = m_{gV} + m_{gL}$
Water	water in aqueous phase (wA)	$N_3 = m_{wA}$

Table 2—Equilibrium conditions for standard black oil model.

Reaction	Equilibrium condition
$gV \leftrightarrow gL$	$\frac{m_{gL}}{m_{oL}} = R_s(P)$

EOS compositional model.

The compositional model allows for more components and changes in hydrocarbon phase composition. The phase pressure/volume/temperature (PVT) properties are calculated through an equation of state (EOS). Viscosities and interfacial tensions are functions of composition, pressure and temperature. The system is well studied in the EOS compositional literature (Coats 1980; Collins et al. 1992; Nghiem et al. 1981). There are three phases (vapor, liquid and aqueous) and n_c components ($n_c - 1$ hydrocarbon components and water). A new compositional relative permeability model can be used to eliminate phase labeling and make relative permeability more robust (Khorsandi et al. 2017). The component and species are shown in Table 3. Table 4 shows the equilibrium conditions.

Table 3—Species – Component relations for EOS compositional model.

Component	Species	Total amount
Hydrocarbon component i ($i = 1, \dots, n_c - 1$)	molecular group i in vapor phase (iV), molecular group i in liquid phase (iL)	$N_i = m_{iV} + m_{iL}$
Water component i ($i = n_c$)	water molecules in aqueous phase (wA)	$N_{n_c} = m_{wA}$

Table 4—Equilibrium conditions for classic EOS fluid model.

Reaction	Equilibrium condition
$iV \leftrightarrow iL$ ($i = 1, \dots, n_c - 1$)	$\log f_{iV} - \log f_{iL} = 0$

Reactive fluid model.

For reactive transport models, a conventional technique to reduce the complexity is to classify the species into the primary and secondary species. A mass conservation equation is written for each primary species while the concentration of the secondary species can be calculated from reaction equilibrium constraints using the primary species concentration. For such systems, the number of components equals the number of species minus the number of reaction constraints, which is the number of primary species. Consider a system with n_s species and n_r ($n_r < n_s$) independent equilibrium chemical reactions, the chemical reactions can be described by the following equation

$$\sum_{j=1}^{n_s} \gamma_{ij} A_j \leftrightarrow 0, \quad i = 1, \dots, n_r$$

where A_j denotes the chemical formula of the j th species. At equilibrium, the mass action law holds

$$\log K_i = \sum_{j=1}^{n_s} \gamma_{ij} \log a_j \quad (5)$$

where K_i is the equilibrium constant at the given pressure and temperature for the i th reaction and a_j is the activity for the j^{th} species. Using vector notation (Saaltink and Ayora 1998), denote

$$\mathbf{k} = (K_1, K_2, \dots, K_{n_r})^T$$

$$\mathbf{a} = (a_1, a_2, \dots, a_{n_s})^T$$

and S_e as a stoichiometric matrix ($n_r \times n_s$),

$$\mathbf{S}_e = \begin{pmatrix} \gamma_{11} & \cdots & \gamma_{1n_s} \\ \vdots & \ddots & \vdots \\ \gamma_{n_r 1} & \cdots & \gamma_{n_r n_s} \end{pmatrix}$$

The equilibrium conditions can be written in n_r dimensions as a vector equation

$$\mathbf{S}_e \log \mathbf{a} = \log \mathbf{k}$$

Since the reactions considered are independent reactions, matrix S_e has a rank of n_r . Therefore, after permutation of the columns, we can always partition the matrix S_e as

$$\mathbf{S}_e = (\mathbf{S}_1 \mid \mathbf{S}_2)$$

where S_1 is $n_r \times (n_r - n_s)$ and S_2 is $n_r \times n_r$ such that S_2 is invertible. Therefore

$$\mathbf{S}_2 \log \mathbf{a}_2 = \log \mathbf{k} - \mathbf{S}_1 \log \mathbf{a}_1 \quad (6)$$

If the secondary species is chosen such that S_2 is an identity matrix, then a_2 can be easily expressed as a function of \mathbf{a}_1 . If not, then

$$\log \mathbf{a}_2 = -(\mathbf{S}_2^{-1} \mathbf{S}_1) \log \mathbf{a}_1 + (\mathbf{S}_2^{-1}) \log \mathbf{k}. \quad (7)$$

In that case, we can redefine the chemical system as

$$\mathbf{S}^* = -(\mathbf{S}_2^{-1} \mathbf{S}_1) \quad (8)$$

$$\mathbf{S}_2^* = \mathbf{I}_{n_r} \quad (9)$$

$$\log \mathbf{k}^* = (\mathbf{S}_2^{-1}) \log \mathbf{k} \quad (10)$$

where \mathbf{I}_{n_r} refers to the identity matrix with rank n_r . The mass action law can be written as

$$\log \mathbf{a}_2 = \mathbf{S}_1^* \log \mathbf{a}_1 + \log \mathbf{k}^*. \quad (11)$$

Therefore, each equilibrium reaction can be written in the canonical form:

$$B_k \leftrightarrow \sum_{i=1}^{n_s - n_r} s_{ki} A_i, k = 1, \dots, n_r,$$

where S_{kj} are the $(k, j)^{\text{th}}$ entry in matrix \mathbf{S}^* . This system has a degree of freedom of $n_r - n_s$, and therefore, this system has $n_c = n_r - n_s$ components. Component i has a total moles of

$$N_i = m_{A_i} + \sum_{k=1}^{n_r} s_{ki} m_{B_k} \quad (12)$$

where N_1, \dots, N_{n_c} are conserved under instantaneous equilibrium reactions. Given N_i , we can compute the moles of each species. The transport solution portion does not need to know the n_r instantaneous reactions, and only views the system as a n_c component system. Kinetic reaction rates are calculated after the equilibrium is reached. The component and species are shown in [Table 5](#). [Table 6](#) shows the equilibrium condition.

Table 5—Species – Component relations for the reactive fluid model.

Component	Species	Total amount
Component i ($i = 1, \dots, n_c$)	primary species i , a group of secondary species k	$N_i = m_{A_i} + \sum_{k=1}^{n_r} s_{ki} m_{B_k}$

Table 6—Equilibrium conditions for the reactive fluid model.

Reaction	Equilibrium condition
$B_k \leftrightarrow \sum_{i=1}^{n_s-n_r} s_{ki} A_i$ $k = 1, \dots, n_r$	$\log a_{B_k} = \sum_{i=1}^{n_s-n_r} s_{ki} \log a_{A_i} + \log k_k^*$

Fluids with phase and reaction equilibrium.

For CO₂ flooding or CO₂ sequestration, there is significant mass transfer between phases, while within the aqueous phase the reactions cannot always be neglected. In such systems, there are equilibrium constraints of multiple types. It would be difficult to add reactions to a conventional gas flooding simulator if the simulator structure is not designed properly. On the other hand, it is difficult to add phase equilibrium conditions into a reactive transport code if the reaction correlations are expressed in the transport equation. The mass conservation equation for each species is not directly usable because reaction rates of the instantaneous reactions cannot be expressed explicitly. This is because the characteristic time of reactions is much smaller than the timescale of the porous media flow. To solve this problem, we redefine the component, using the configuration of a reactive model, such that the total moles of a component is conserved under instantaneous phase and reaction equilibrium. Therefore, the numerical solution of external flow parts can be coded without any knowledge of the complex reactions.

The phase equilibrium can be represented in a reaction form

molecule (phase 1) \leftrightarrow molecule (phase 2).

The only difference is the equilibrium condition. We can use an extended stoichiometric matrix to organize the reaction and phase equilibrium relations. The reaction and phase equilibrium system can be described by the following equation

$$B_k \leftrightarrow \sum_{i=1}^{n_s-n_r} s_{ki} A_i, k = 1, \dots, n_r + n_{pheq}$$

where n_r is the number of reactions and n_{pheq} is the number of phase equilibrium relations. The component and species are shown in Table 7. Table 8 shows the equilibrium condition.

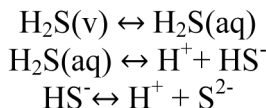
Table 7—Species – Component relations for multiphase reactive fluid model.

Component	Species	Total Amount of the Component
Component i ($i = 1, \dots, n_c$)	primary species i , a group of secondary species k	$N_i = m_{A_i} + \sum_{k=1}^{n_r} s_{ki} m_{B_k}$

Table 8—Equilibrium condition for multiphase reactive fluid model.

Reaction	Equilibrium condition
$B_k \leftrightarrow \sum_{i=1}^{n_s-n_r} s_{ki} A_i$ $k = 1, \dots, n_r + n_{pheq},$	$\log a_{B_k} = \sum_{i=1}^{n_s-n_r} s_{ki} \log a_{A_i} + \log k_k^*$ <p>when the k^{th} reaction is dominated by mass action; log</p> $f_{B_k} = \sum_{i=1}^{n_s-n_r} s_{ki} \log f_{A_i}$ <p>when the k^{th} "reaction" is dominated by fugacity equality.</p>

One example of such a system is for sour gas, where the following phase and chemical equilibrium holds:



The species in this system includes $\text{H}_2\text{S}(\text{v})$, $\text{H}_2\text{S}(\text{aq})$, H^+ , HS^- , S^{2-} and $\text{H}_2\text{O}(\text{aq})$. For simplicity, we do not consider water vaporization in the example. In canonical form, the reaction matrix can be written as

Species	$\text{H}_2\text{S}(\text{v})$	H^+	S^{2-}	$\text{H}_2\text{S}(\text{aq})$	HS^-	H_2O
Reaction 1	1			-1		
Reaction 2		1		-1	1	
Reaction 3			1	1	-2	

where the empty spaces are zeros. The stoichiometry matrix \mathcal{S}^* can be written as

Species	$\text{H}_2\text{S}(\text{aq})$	HS^-	H_2O
$\text{H}_2\text{S}(\text{v})$	1		
H^+	1	-1	
S^{2-}	-1	2	

The equilibrium conditions are

$$\log f_{\text{H}_2\text{S}(\text{v})} = \log f_{\text{H}_2\text{S}(\text{aq})}$$

$$\log a_{\text{H}^+} = \log a_{\text{H}_2\text{S}(\text{aq})} - \log a_{\text{HS}^-} + \log k_2$$

$$\log a_{\text{S}^{2-}} = -\log a_{\text{H}_2\text{S}(\text{aq})} + 2 \log a_{\text{HS}^-} + \log k_3$$

Here we have three primary species, namely $\text{H}_2\text{S}(\text{aq})$, HS^- and $\text{H}_2\text{O}(\text{aq})$, and three components represented by those three species. The total moles of each component are

$$N_1 = m_{\text{H}_2\text{S}(\text{aq})} + m_{\text{H}_2\text{S}(\text{v})} + m_{\text{H}^+} + m_{\text{S}^{2-}}$$

$$N_2 = m_{\text{HS}^-} - m_{\text{H}^+} + 2m_{\text{S}^{2-}}$$

$$N_3 = m_{\text{H}_2\text{O}(\text{aq})}$$

The defined component quantities N_1 , N_2 and N_3 are conserved under the instantaneous phase and chemical equilibria. Note that here the unit conversion between different systems needs special attention. The calculated ω_{ij} are the molar density of component i in phase j , which only count in the species in the same phase. For this example, we have vapor and aqueous phases, and therefore

$$\begin{aligned}
\omega_{1,v} &= \frac{m_{H_2S(v)}}{\text{vapor phase volume}} \\
\omega_{1,aq} &= \frac{m_{H_2S(aq)} + m_{H^+} + m_{S^{2-}}}{\text{aqueous phase volume}} \\
\omega_{2,v} &= 0 \\
\omega_{2,aq} &= \frac{m_{HS^-} - m_{H^+} + 2m_{S^{2-}}}{\text{aqueous phase volume}} \\
\omega_{3,v} &= 0 \\
\omega_{3,aq} &= \frac{m_{H_2O}}{\text{aqueous phase volume}}
\end{aligned}$$

The phase total molar density ω_{ij} is only used in the phase flow equation and usually does not correspond to a specific species mole fraction.

Surfactant fluids with reactions.

Geochemical reactions play an important role in chemical flooding, since the performance of the surfactant and polymer depends on the pH, ionic composition and total ionic strength of the solution (Luo et al. 2016). Here, using our framework, we couple a surfactant phase behavior model to the general framework, instead of developing a new code.

In surfactant polymer fluids, three phases are defined: oleic phase (O), micro-emulsion phase (M) and aqueous phase (W). The oleic and aqueous phases are assumed to be free of surfactant for simplicity. The micro-emulsion phase is a mixture of the oleic phase and aqueous phase where the oleic/aqueous phase is assumed to have the same composition with the separated oleic/aqueous phase. The geochemical reactions do not involve surfactant, oil or water molecules. Therefore the equilibrium chemical reaction and the phase equilibrium mass transfer are independent. Table 9 and Table 10 shows the definition of total moles and the equilibrium conditions.

Table 9—Species – Component relation for surfactant model.

Component	Species	Total Amount of the Component
Oil	oil in the oleic phase oil in the micro-emulsion phase	$N_1 = m_{oO} + m_{oM}$
Water	water in the aqueous phase water in the microemulsion phase	$N_2 = m_{w,M} + m_{w,W}$
Surfactant	surfactant in the microemulsion phase	$N_3 = m_{surfactant,m}$
Aqueous component i ($i = 4, \dots, n_c$)	primary species p_i , a group of secondary species q_k	$N_i = m_{A_i} + \sum_{k=1}^{n_r} s_{ki} m_{B_k}$

Table 10—Equilibrium condition for surfactant system with chemical reactions.

Reaction	Equilibrium condition
$oO \leftrightarrow oM$	$\frac{m_{oM}}{m_{sM}} = \sigma(HLD)$
$wW \leftrightarrow wM$	$\frac{m_{wM}}{m_{sM}} = \sigma(HLD)$
$B_k \leftrightarrow \sum_{i=1}^{n_s-n_r} s_{ki} A_i$ $k = 1, \dots, n_r$	$\log a_{B_k} = \sum_{i=1}^{n_s-n_r} s_{ki} \log a_{A_i} + \log k_k^*$

Other enhanced oil recovery models like polymer and alkali flooding can be put into a general compositional model similarly. For example, polymer flooding can be written in compositional form by adding one additional component (polymer, such as shown in Khorsandi et al. (2016a)) and their effects on properties like viscosity.

Results and Validation

PennSim, our in-house simulation software at Penn State, is a C++ implementation of the general framework coupled to a suite of fluid models. In the following, we compare PennSim with commercial simulators such as Eclipse 300 (ECL300) and CMG-GEM for accuracy and performance. In the following, the simulators were not tuned to give an optimum performance for each specific case.

Case 1: First SPE Comparative Project.

Here, the first SPE comparative project (Odeh 1981) is used for comparison with other codes. This problem is a three-phase black oil simulation of a quarter of a five-spot pattern. Different layers have different porosity and permeability. The fluid model is the classic black oil model with variable bubble point pressure. The details of this simulation case study can be found in Odeh (1981). The flow solver is FIM. The field average pressure and bottom hole pressure of the producer is shown in Figure 2 in comparison with Eclipse 300. PennSim matches Eclipse 300 well for all cases considered.

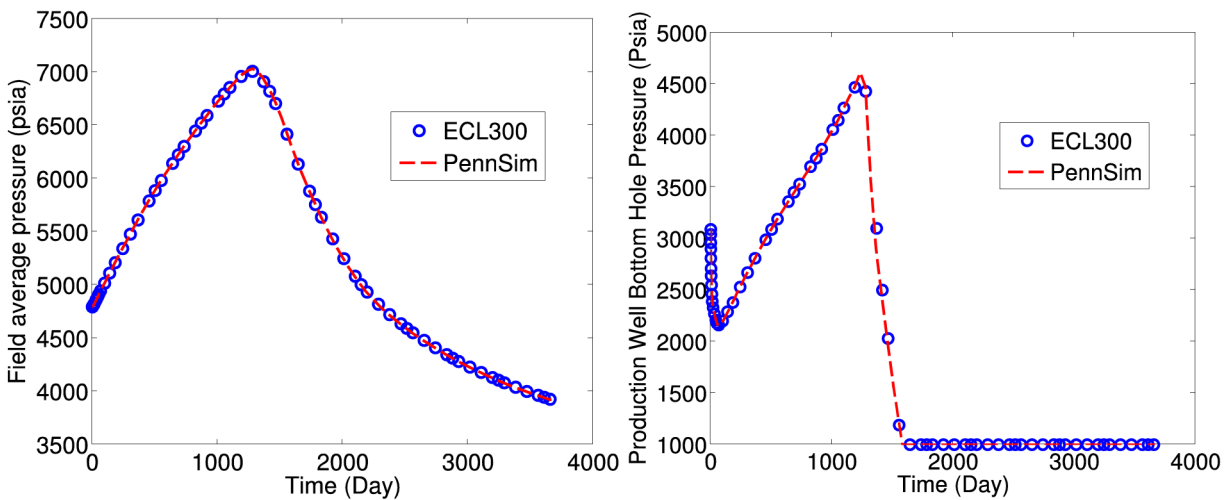


Figure 2—Comparison of SPE 1 simulation results using PennSim and Eclipse 300.

Case 2: Ninth SPE Comparative Project.

The ninth SPE comparative project (Killough 1995) is known to be difficult because of the discontinuous relative permeability and capillary pressure curves. This displacement provides a re-examination of the black oil model with 9000 cells and with a high degree of heterogeneity. There is one injection well and 25 production wells. Other details of the simulation model can be found in Killough (1995). The average field pressure and oil production rate for the first producer from PennSim and Eclipse 300 is shown in Figure 3. Those comparisons show that PennSim matches with Eclipse 300 well.

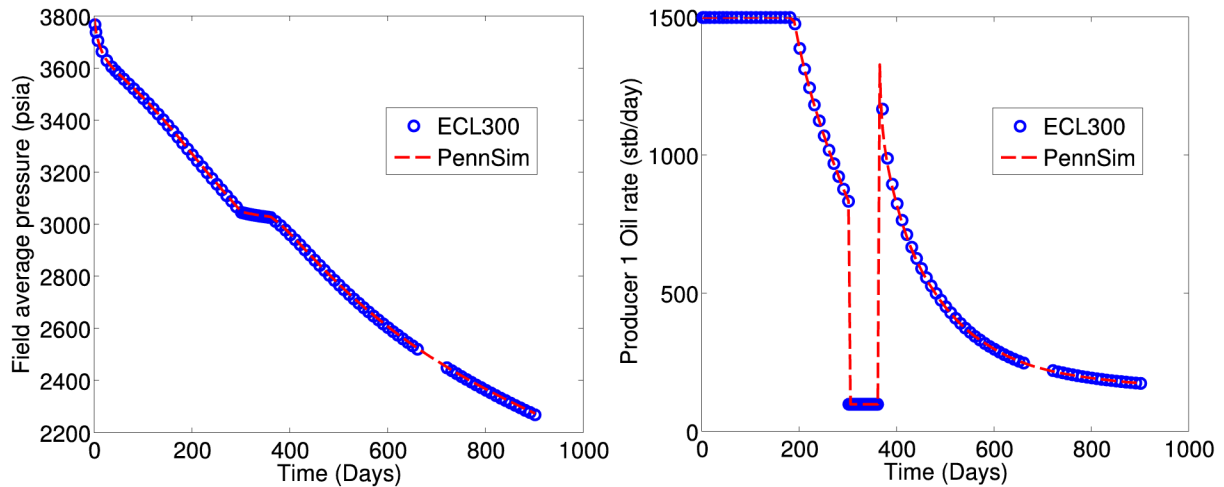


Figure 3—Comparison of SPE 9 simulation results using PennSim and Eclipse 300.

Case 3: Upscaled Tenth SPE Comparative Project.

SPE 10 is a large heterogeneous two phase model (Christie et al. 2001) that simulates a waterflood. The original model has over one million grid blocks and strong heterogeneity. Because Eclipse could not finish the simulation within a reasonable time, we used a model with only 30 thousand grid blocks whose permeability and porosity is upscaled from the original SPE10 problem. More details of the SPE10 comparative solution project can be found in Christie et al. (2001). Figure 4 shows the field average pressure and injection well bottom hole pressure calculated by PennSim and Eclipse. The simulation results of PennSim and Eclipse 300 agree nearly exactly. The computational time is 75 seconds for PennSim and 652 seconds for ECL300.

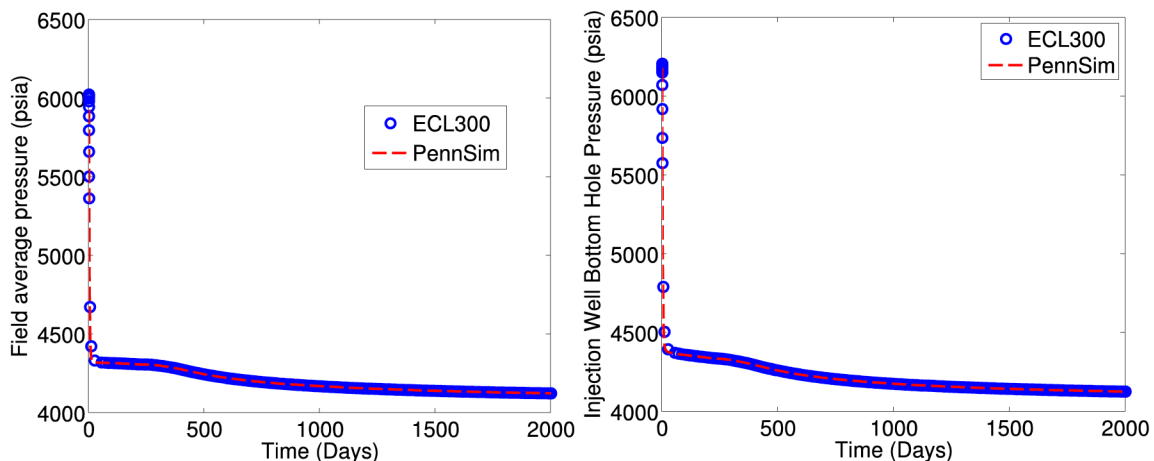


Figure 4—Comparison of upscaled SPE 10 simulation results using PennSim and Eclipse 300.

Case 4: A mature field in Europe.

This more realistic model uses a black oil model with immiscible oil and water phases. Corner point grid is used with 614,040 grid blocks and 89 wells. There are 10 saturation regions with 10 sets of relative permeability/capillary pressure. Well multipliers are used to history match the well data. ECL100 was used due to the original input data format. The first 1500 days simulation was compared with ECL100. The production rates of three wells are shown in Figure 5. The PennSim results agree well with Eclipse 100. Moreover, for the first 1500 days, PennSim takes about two-thirds of the computational time of ECL100.

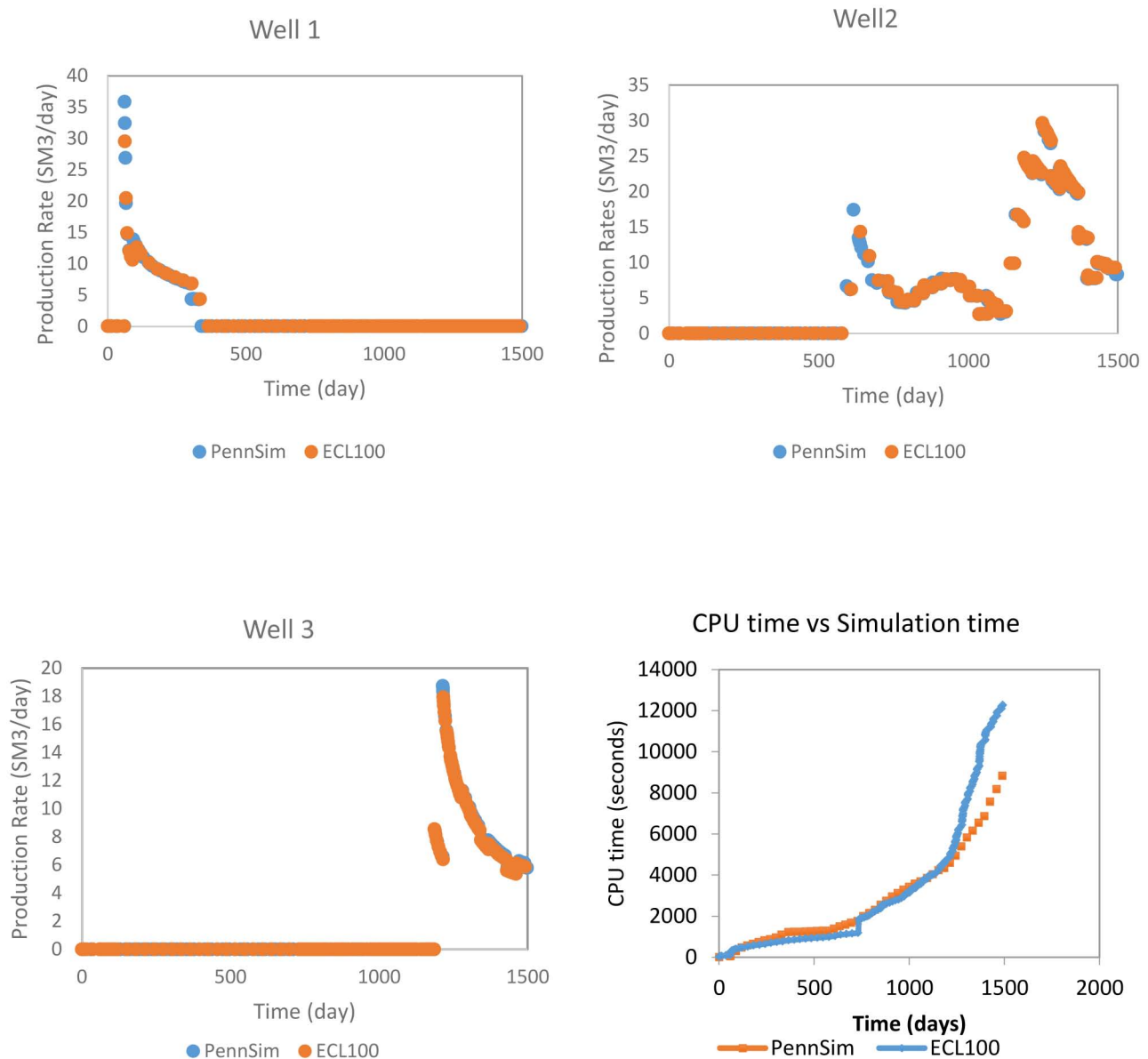


Figure 5—Comparison of a mature oil field simulation results using PennSim and Eclipse 100.

Case 5: Fifth SPE Comparative Project - Water Alternating Gas Injection.

The fifth SPE comparative solution project (Killough et al. 1987) is a three-dimensional case with nonzero capillary pressure. The reservoir is discretized into $7 \times 7 \times 3$ grid blocks with heterogeneous permeability. The six component EOS model in Killough et al. (1987) is used. The reservoir temperature is F. Here the injection and production well condition are modified since the current version of PennSim is not coupled with surface facilities. Therefore, instead of using a constant surface volumetric rate, the production well

is operated at constant bottom hole pressure of 3800 psia. The solvent is injected at 31792 lb-mol/day in the gas cycle. In the water cycle, water is injected at 12000 stb/day. More details of SPE5 can be found in Killough et al. (1987). The injection well block pressure and the production rate of C_6 is shown in Figure 6. These figures indicate that PennSim matches CMG-GEM well for the three-dimensional heterogeneous WAG simulation.

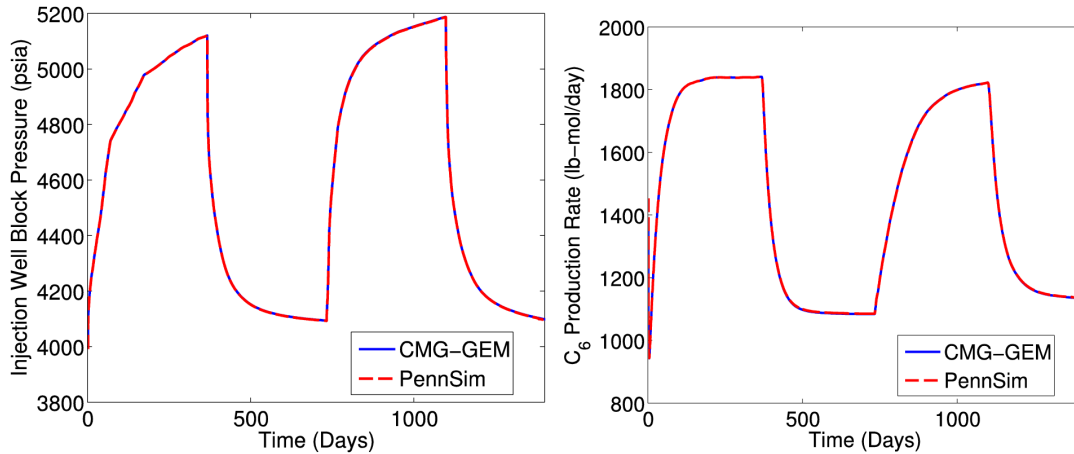


Figure 6—Comparison of modified SPE 5 simulation results using PennSim and CMG-GEM.

Case 6: Multi-Mineral Alteration Reactive Transport Model.

One case with seven reactions are simulated and compared with CrunchFlow (Steefel 2009). Here we consider a single phase reactive transport model. The considered mineral reactions are shown in Table 11. The reaction kinetics parameters can be found in Table 12. Table 9 shows the initial and injection concentration of the primary species. The comparison of PennSim with CrunchFlow can be found in Figure 7. An excellent match is obtained between PennSim and CrunchFlow.

Table 11—Mineral reactions and equilibrium constants used in Case 6.

Mineral reactions	Equilibrium constant
Calcite + H^+ \leftrightarrow Ca^{2+} + HCO_3^-	$\log(K_{eq})=1.8542$
Quartz \leftrightarrow $SiO_2(aq)$,	$\log(K_{eq})=-4.0056$
Magnesite + H^+ \leftrightarrow Mg^{2+} + HCO_3^- ,	$\log(K_{eq})=2.2985$
Dolomite + $2H^+$ \leftrightarrow Ca^{2+} + Mg^{2+} + $2HCO_3^-$,	$\log(K_{eq})= 2.5135$
Kaolinite+ $6H^+$ \leftrightarrow $5H_2O$ + $2SiO_2(aq)$ + $2Al^{3+}$,	$\log(K_{eq})=5.4706$
Illite+ $8H^+$ \leftrightarrow $5H_2O$ + $0.25Mg^{2+}$ + $0.6K^+$ + $2.3Al^{3+}$ + $3.5SiO_2(aq)$	$\log(K_{eq})=9.0260$
Anorthite + $8H^+$ \leftrightarrow Ca^{2+} + $2Al^{3+}$ + $2SiO_2(aq)$	$\log(K_{eq})=26.53$

Table 12—The parameters for kinetic mineral reactions used in Case 6.

Mineral	Rate constant (mol/m ² s)	Specific surface area	Volume fraction
Calcite	-6.19	0.05	0.01
Quartz	-35	0.35	2.5
Magnesite	-5.18	0.02	0.1
Dolomite	-9.221	0.01	2.5
Kaolinite	-13	0.01	2500
Illite	-14	0.01	2500
Anorthite	-12	0.01	2500

Table 13—The initial and inlet concentrations of the components in Case 6.

species	H ⁺	HCO ₃ ⁻	Cl ⁻	Na ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	SiO ₂ (aq)	K ⁺
initial	1.00E-7	8.20E-8	1E-7	1E-7	1E-7	1E-7	3.93E-11	1E-20	1E-7
inlet	1E-4	4.54E-7	1E-7	1E-7	1E-7	1E-7	9.98 E-8	1E-20	1E-7

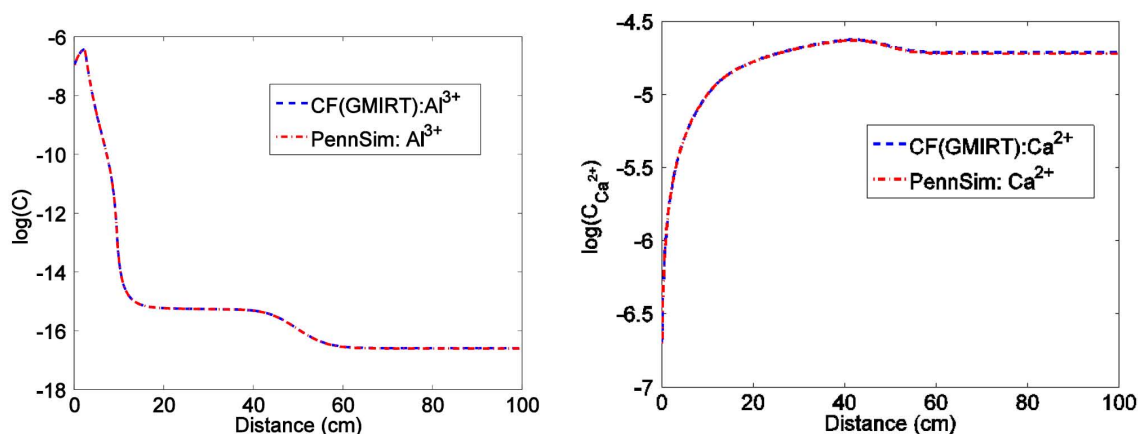


Figure 7—Comparison of case 6 results using PennSim and CrunchFlow.

Our framework has also been used to simulate coupled processes such as mineral dissolution in CO₂ WAG flooding (Qiao et al. 2015), polymer flooding (Khorsandi et al. 2016a), surfactant-polymer flooding (Khorsandi et al. 2016b) and injection of surfactant mixtures with selective adsorption (Magzymov et al. 2016). These papers give comparisons to analytical and numerical models as well, further validating the framework.

Conclusion

In this paper, we unified different models into a general component mass conservation equation and the constitutive laws to form a closed set of local equations that includes the coupling of local mass conservation through phase equilibrium and reaction equilibrium.

- The significant advantage of this framework is that the flow portion is coded only once, as long as the transport mechanisms (namely Darcy's law) holds. Also, the development between discretization and phase behavior reactions can be separated into modules.

- We implemented models for black oil, complex composition processes using a cubic equation of state, reactive transport, coupled CO₂ dissolution and reaction, and chemical flooding. The simulation results match well with commercial simulators and shows improved speed.

We clarified the notation and code structure so that a large code is maintainable. The limitation of this framework now is that the energy balance equation is not added.

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