Parameterization of element balance formulation in reactive compositional flow and transport

Kala, Keshav; Voskov, Denis; Ammiwala, Mohammad Huzefa

DOI

[10.2118/193898-MS](https://doi.org/10.2118/193898-MS)

Publication date

2019

Document Version

Final published version

Published in

Society of Petroleum Engineers - SPE Reservoir Simulation Conference 2019, RSC 2019

Citation (APA)

Kala, K., Voskov, D., & Ammiwala, M. H. (2019). Parameterization of element balance formulation in reactive compositional flow and transport. In S. Alnuaim (Ed.), *Society of Petroleum Engineers - SPE Reservoir Simulation Conference 2019, RSC 2019* [SPE-193898-MS] Society of Petroleum Engineers. <https://doi.org/10.2118/193898-MS>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

Green Open Access added to TU Delft Institutional Repository

'You share, we take care!' - Taverne project

<https://www.openaccess.nl/en/you-share-we-take-care>

Otherwise as indicated in the copyright section: the publisher is the copyright holder of this work and the author uses the Dutch legislation to make this work public.

Society of Petroleum Engineers

SPE-193898-MS

Parameterization of Element Balance Formulation in Reactive Compositional Flow and Transport

Keshav Kala, TU Delft; Denis Voskov, TU Delft, Stanford University; Mohammad Huzefa Ammiwala, TU Delft

Copyright 2019, Society of Petroleum Engineers

This paper was prepared for presentation at the SPE Reservoir Simulation Conference held in Galveston, Texas, USA, 10–11 April 2019.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

A novel formulation for modeling nonlinear reactive-compositional transport comprising of complex phase behaviors with chemical and thermodynamic interactions is presented. The precipitation/dissolution of minerals during reactive flow in subsurface reservoirs is modeled in the newly designed simulation framework. This framework uses molar formulation with a consistent reduction of governing mass balance equations from component to element mole fractions. The thermodynamic phase behaviour is extended by including the chemical equilibrium reactions in the multiphase thermodynamic flash. This allows for a general treatment of chemical and thermodynamic equilibrium in a fully couple and implicit manner. The governing component conservation equations are reduced to element conservation equations using the Equilibrium Rate Annihilation matrix. The element composition of the mixture serves as an input for these computations whereas the output is fractions of components in each phase, including solids. To solve the resulting nonlinear element based governing equations, we use the Adaptive Operator-Based Linearization (OBL) approach where the governing equations are formulated in terms of space and state-dependent parameters. The proposed framework is utilized for modeling of several challenging flow and transport problems with dissolution and precipitation reactions. This is the first time when a multiphase multicomponent flash using element fractions as an input is coupled with an element balance compositional formulation and validated for multidimensional problems of practical interest. In addition, an efficient parametrization using adaptive OBL approach improves both robustness and performance of complex reactive-compositional flow and transport.

Introduction

Reservoir simulation is an important tool for effective reservoir management. Therefore, continuous efforts are made to improve the performance and accuracy of simulators. Complex multi-component mixture can be separated into gas, liquid, aqueous and solid phase based on thermodynamic properties including pressure and temperature. Along with the in-situ reservoir fluid, other components can also be injected into the reservoir during its life-cycle in order to achieve maximum recovery (Lake, 1989). The distribution of different components in various phases is controlled by thermodynamic equilibrium, chemical equilibrium, and chemical kinetics which are strong functions of pressure, temperature and composition. Therefore, for

accurate modeling of such systems, one needs to couple these effects with flow and transport which requires solving multiple nonlinear governing equations.

One of the first efforts to couple chemical reactions with flow has been performed by [Lichtner \(1985\)](#). He reduced the species into primary and secondary components and decoupled the local chemical equilibrium reactions from the solution of single-phase flow ([Lichtner et al., 1996](#)). In the traditional compositional simulation, the coupling of chemical and thermodynamic equilibria becomes quite complex, and phase behavior can take a significant portion of computational time due to the potential presence of multiple phases. Using the Gibbs Energy minimization technique proposed by [Michelsen \(1982\)](#), reservoir simulation procedure determine the phase state and consequently run flash calculations if required. [Rachford and Rice \(1952\)](#) formulated a single equation which solves for phase fractions and phase compositions in multiphase systems given the partition coefficient values. [Li and Nghiem \(1982\)](#) allowed the phase fractions to become negative which indicates the presence of single-phase mixture and later [Whitson and Michelsen \(1989\)](#) bounded the range of vapor fraction values. The sub-critical single-phase region can be uniquely identified by tie-lines and the negative flash procedure ([Iranshahr et al., 2010](#)) can be used in combination with tie-line parametrization technique [Iranshahr et al. \(2013\)](#) for an effective phase-state identification method which does not require a stability test.

[Yeh and Tripathi \(1989\)](#) studied different approaches to couple chemical reactions with transport and then suggested the Sequential Iterative approach (SIA) to model the reactive transport. [Fan \(2010\)](#) introduced coupling between compositional transport and chemical reactions in a fully implicit manner. He applied the element based formulation which was later extended by [Farshidi et al. \(2013\)](#) to capture multiple equilibria and kinetic reactions using both natural and molar based formulations. [Nghiem et al. \(2011\)](#) also demonstrated element and species balance formulation for chemical reactions in an aqueous phase. [Voskov et al. \(2017\)](#) incorporated the Gibbs-Helmholtz constrained (GHC) equation of state solver ([Lucia et al., 2015](#)) for simultaneous solution of thermodynamic and chemical equilibrium in the natural formulation to model multiple salt precipitation/dissolution reactions. This approach was implemented in the Automatic Differentiation General Purpose Research Simulation (AD-GPRS) framework ([Garipov et al., 2018](#)).

However, all of these approaches uses loose coupling between thermodynamic and chemical equilibrium which affects the robustness and efficiency of simulation. The rigorous coupling of thermodynamic equilibrium in the presence of chemical reactions is a challenging task due to the sensitivity of partial derivatives in global fully-implicit Jacobian to changes controlled by nonlinear equilibrium constraints. In this study, we present the first fully coupled approach using a recently developed fully-implicit Operator-Based Linearization (OBL) technique proposed in [Voskov \(2017\)](#). The OBL method controls the nonlinearity of the problem with the multilinear representation of state-dependent operators in governing equations. During the course of the simulation, these operators are interpolated in parameter space with a predefined accuracy. The values of the state operators are calculated adaptively using conventional property estimators based on various correlations and solution of Equation of State ([Khait and Voskov, 2017](#)).

In this paper, we show a brief description of the algebraic framework to solve the reactive flow and transport problem. The first section describes governing equations for multiphase compositional simulation in chemical and thermodynamic equilibrium assumptions. In the second section, we briefly explain the reduction of governing equations to element formulation (for more detailed derivations see [Kala and Voskov, 2018](#)). The third section describes the simultaneous solution of thermodynamic and chemical equilibrium using an extended negative flash technique and includes an illustrative example. The last section presents several simulation examples used to test and validate the developed framework. The proposed approach is implemented in Delft Advanced Research Terra Simulator ([DARTS, 2019](#)).

Conventional governing equations

We first look at the conventional mass balance equation in traditional reactive compositional based flow and transport systems.

Conservation of species

The basic mass balance equations taking into account chemical reactions in the source/sink term following Lake (1989) is shown below

$$\frac{\partial n_i}{\partial t} + l_c + q_c = \sum_{k=1}^K v_{ck} r_k + \sum_{q=1}^Q v_{cq} r_q, \quad c = 1, \dots, C, \quad (1)$$

where n_c is the mass of component, l_c is the total flux of the component, v_{ck} is the stoichiometric coefficient of kinetic reaction k for the component c and v_{cq} is the stoichiometric coefficient for equilibrium reaction, r_q is the equilibrium reaction rate and r_k is the kinetic reaction rate. n_c here is defined as given below

$$n_c = \phi \sum_{j=1}^P (\rho_j s_j x_{cj}) + \sum_{l=1}^M (1 - \phi) \rho_l x_{cl}, \quad c = 1, \dots, C. \quad (2)$$

P is the total number of fluid phases present and M is total solid phases. Combining the first and second terms in (2) yields the total amount of component present in solid and fluid phases. The term l_c defines the flux of component c and is given as:

$$l_c = \nabla \sum_{j=1}^P (\rho_j x_{cj} \mathbf{u}_j) + \rho_j \phi s_j d_{cj} \nabla x_{cj}, \quad c = 1, \dots, C, \quad (3)$$

where the term d_{cj} corresponds to the dispersion of component c in phase j . For simplicity, this term is neglected in our study. The term $\mathbf{u}_j$ is the velocity of the phase j and is defined by Darcy's law:

$$\mathbf{u}_j = -\mathbf{K} \frac{k_{rj}}{\mu_j} (\nabla p - \rho_j g \nabla d) \quad (j = 1, \dots, P). \quad (4)$$

The rest of the properties are split into the state dependent (ω) and space dependent (ξ) relations.

- State dependent (fluid and rock interactions):
 - $k_{rj}(\omega)$ - relative permeability,
 - $s_j(\omega)$ - saturation,
 - $x_{cj}(\omega)$ - molefraction of component c in phase j .
- Space dependent (properties altered in space):
 - ϕ, ξ - porosity,
 - $\mathbf{K}(\omega, \xi)$ - permeability tensor,
 - $\mathbf{u}_j(\omega, \xi)$ - permeability tensor,

Since we are considering that the solid phase is not moving, the flux term associated with the solid phase is equal to zero. Eq. 1 can now be simplified and transformed to a vector form as:

$$\frac{\partial \mathbf{n}}{\partial t} + \mathbf{l} + \mathbf{q} = \mathbf{V} \mathbf{r}, \quad (5)$$

where $\mathbf{n} = (n_1, \dots, n_C)^T$, $\mathbf{l} = (l_1, \dots, l_C)^T$, $\mathbf{V}$ is the stoichiometric matrix in a reaction and $\mathbf{r} = (r_1, \dots, r_Q)^T$.

Closing assumptions

For the closure of the system, we use the chemical and thermodynamic equilibrium relations. Chemical Equilibrium is defined as reactions which have their forward reaction rate similar to the rate of backward reaction. For equilibrium reactions, instantaneous local equilibrium is assumed due to high reaction rates and their reversible nature. Chemical equilibrium is given by the law of mass action as:

$$Q_q - K_q = \prod_{c=1}^C \alpha_c^{v_{cq}} - K_q = 0. \quad (6)$$

Here Q_q is the reaction quotient whereas K_q is the equilibrium reaction quotient or equilibrium solubility limit in case of dissolution/precipitation of minerals.

Next, we look into thermodynamic equilibrium relations which are governed by equality of fugacity in different phases. A component is at thermodynamic equilibrium if the chemical potentials of the component in both phases are equal. Numerically, it can be written as

$$f_{i1} - f_{ij} = 0, \quad i = 1, \dots, C, \quad j = 2, \dots, P. \quad (7)$$

These fugacity relation can also be written in terms of partition coefficients (K)

$$Kx_{i1} - x_{ij} = 0, \quad i = 1, \dots, C, \quad j = 2, \dots, P. \quad (8)$$

The two methods to predict the thermodynamic phase behavior are EOS-based and constant K-values-based methods, see [Zaydullin et al. \(2017\)](#) for comparisons and details. The EOS-based methods use iterative procedures to solve the cubic EOS (e.g. [Peng and Robinson, 1976](#)), until the fugacity constraint is satisfied. Whereas constant K-value flash assumes partition coefficients are only functions of pressure and temperature. For simplicity in this study, we use the constant K-value-based approach. The remaining thermodynamic closing relations are given below

$$z_i - \sum_{j=1}^P x_{ij} v_j = 0, \quad i = 1, \dots, C, \quad (9)$$

$$\sum_{i=1}^C x_{i1} - \sum_{i=1}^C x_{ij} = 0, \quad j = 2, \dots, P, \quad (10)$$

$$\sum_{j=1}^P v_j - 1 = 0, \quad j = 1, \dots, P, \quad (11)$$

where v_j is defined as

$$v_j = \frac{\rho_j s_j}{\sum_{k=1}^P \rho_k s_k}, \quad j = 1, \dots, P. \quad (12)$$

Equation (9) is the local mass balance for the component c in fluid, equations (10) is the phase composition constraint, and equation (11) is the phase fraction constraint.

Nonlinear formulation

Different nonlinear formulations like: (1) natural formulation ([Coats, 1980](#)) and (2) molar formulation ([Acs et al., 1985](#); [Collins et al., 1992](#)), are used in reservoir simulation community. An extended analysis of the different types of formulations has been covered in [Voskov and Tchelepi \(2012\)](#).

The governing equations (1) in the molar formulation are solved for pressure (p) and overall composition (z) where the overall molar mass of component in (1) can be written as

$$n_c = \phi \rho_t z_c + \sum_{l=1}^M (1 - \phi) \rho_l x_{cl}, \quad c = 1, \dots, C, \quad (13)$$

where ρ_t is the total density of the fluid. The set of secondary equations (8) to (11) are solved iteratively in multiphase flash procedure. The primary mass balance governing equations are linearized using the Newton-Raphson approach given as

$$J(\mathbf{y}^k)(\mathbf{y}^{k+1} - \mathbf{y}^k) = -\mathbf{r}(\mathbf{y}^k). \quad (14)$$

Here J is the Jacobian matrix containing derivatives with respect to primary unknowns, y is a vector of non-linear unknown which are pressure and overall compositions, k is the non-linear iteration and r is the residual of the mass balance equations (5). These linear equations are solved in every nonlinear iteration to obtain an update of primary unknowns. Once the residual is below the tolerance, the system is converged, and the Newton loop is terminated. The derivatives of secondary variables with respect to the primary nonlinear unknowns can be calculated in this case using the inverse theorem (Voskov and Tchelepi, 2012).

Element balance reduction

Here we briefly explain the reduction of component mass balance equations to element-based mass balance equations with thermodynamic and chemical equilibria decoupled from the governing equations. We begin with taking a simple chemical equilibrium reaction for halite dissolution and precipitation in an aqueous solution which is given as:

The addition of chemical reactions to compositional transport is a challenging task due to the following reasons. Firstly, the instantaneous nature of chemical equilibrium reaction makes the transport problem very stiff. Secondly, kinetic and equilibrium reactions are functions of concentrations which are in turn functions of transport which makes the system highly nonlinear. Therefore we formulate the robust element based formulation to resolve this coupling.

Reduction to element conservation

To reduce the system of component-based mass balance equations (5) to element-based equations, we use the Equilibrium rate annihilation matrix (E) and the Stoichiometric matrix (S). The E matrix can be visualized as the distribution of chemical elements in different components and can be written in the matrix form as

$$\mathbf{E} = \begin{bmatrix} & H_2O & CO_2 & Na^+ & Cl^- & NaCl \\ H_2O & 1 & 0 & 0 & 0 & 0 \\ CO_2 & 0 & 1 & 0 & 0 & 0 \\ Na^+ & 0 & 0 & 1 & 0 & 1 \\ Cl^- & 0 & 0 & 0 & 1 & 1 \end{bmatrix}.$$

The rows of the E matrix are chemical elements which combine to form the components. These elements are the smallest chemical species which do not disassociate into the smaller entities. The column of matrix E represents the components involved in the system.

The stoichiometric matrix takes into account the mass balance of components in chemical reactions. The rows of the matrix represent the components involved in the chemical reaction, whereas the columns represent the chemical reactions itself.

$$\mathbf{S} = [0 \quad 0 \quad 1 \quad 1 \quad -1]^T.$$

A detailed explanation of the formulation of $\mathbf{E}$ and $\mathbf{S}$ matrix for a carbonate dissolution/precipitation system is given in [Kala and Voskov \(2018\)](#). Development of general form of Equilibrium rate annihilation matrix and Stoichiometric matrix can be found in [Farshidi et al. \(2013\)](#).

Next, we formulate the element balance equations as suggested in [Sriyanong \(2013\)](#) and write the system of governing equations in terms of mole fractions of elements. To achieve this goal, we pre-multiply the [equation \(5\)](#) with $\mathbf{E}$ which yields the element balance equation

$$\frac{\partial(\mathbf{E}\mathbf{n})}{\partial t} + \mathbf{E}\mathbf{I} = 0 \quad (15)$$

The resulting element based mass balance equation can be re-formulated in terms of element mole fractions ($\mathbf{z}^E$) as shown below

$$\frac{\partial \phi \rho_T^E \mathbf{z}^E}{\partial t} + \mathbf{E}\mathbf{I} = 0. \quad (16)$$

A more detailed derivation of this reduction to element-based mass balance equation can be found in [Kala and Voskov \(2018\)](#). The additional E unknowns $\mathbf{z}^E$ introduced here are closed by additional element to component transformation equations given as

$$\mathbf{z}^E \sum_{c=1}^C \sum_{e=1}^E e_{ec} z_c - \mathbf{E}\mathbf{z} = 0. \quad (17)$$

Flux terms, which formulated in terms of component compositions in each phase, can be determined from the extended flash solver. Since the system of conservation [equations \(5\)](#) is reduced to [\(15\)](#), the chemical equilibrium relations should be included into multiphase flash together with local element-to-component transformation [equations \(17\)](#). The unknown variable set for the element formulation is given below:

$$\gamma_c = \{p, \mathbf{z}^E, \mathbf{z}, v_j, x_{cj}\}, \quad e = 1, \dots, E, \quad c = 1, \dots, C, \quad j = 1, \dots, P.$$

There are in total $E + C + P + C + P + 1$ unknowns in this formulation which are closed by E element conservation equation and Q equilibrium relations which together adds up to C . Then there are E element to component transformation relations [\(17\)](#), $C(P - 1)$ fugacity relations, C overall mole-fraction relation, $P - 1$ phase composition relations, one phase constraint and overall mole-fraction relations. So adding all of them up, the total number of equations becomes $C + E + C + P + P + 1$ which is equal to the total number of unknowns.

Element reduction in Operator Based Linearization

Above, we have discussed how the thermodynamic and chemical equilibrium can be resolved in a coupled manner. Here, we couple phase behavior with the transport solver and complete our reactive-compositional model. In this section, we will first give a short description of parameterization of the governing equation in OBL and generate physics-based operators for one reaction test case.

Conventional OBL

The OBL framework is now extended to solve reactive transport problems along with compositional and geothermal problems ([Khait and Voskov, 2018a,b](#)). OBL allows a flexible solution of nonlinear formulations which have complex derivatives in a fully implicit manner. Determining derivatives of nonlinear element-based equations with respect to $\mathbf{z}^E$ is non trivial therefore solving them with OBL reduces this complexity. The parameterized form of the conventional mass-balance equation for a non-reactive case is first given as

$$a(\xi)(\alpha_c(\omega) - \alpha_c(\omega_n)) - \sum_l \beta_c^l(\omega) b^l(\omega, \xi) = 0, \quad (18)$$

where ω is a state dependent parameter, ξ is a space dependent parameter and operators defined as

- $\alpha_c(\omega) = [1 + c_r(p - p_{ref})]z\rho_T$
- $a(\xi) = V(\xi)\phi_o(\xi)$
- $\beta_c(\omega) = \sum_p x_{c,j} \rho_j \frac{k_{r,j}}{\mu_j}$
- $\beta_c(\omega) = \sum_p x_{c,j} \rho_j \frac{k_{r,j}}{\mu_j}$

Here α and β are state-dependent operators. The value α and β is determined for parametrized set of p and z points which are known as base nodes or nodal values. During the course of the simulation, the operators are interpolated using multi-linear interpolation in parameter space. We use the adaptive extension of OBL as proposed in [Khait and Voskov \(2018b\)](#) where the values of operators are parameterized in the process of a simulation run.

Adding chemical reactions in OBL

We now parameterize the element-based governing equation using alpha and beta operators. We modify the conventional OBL operators to include the chemical equilibrium reactions. The element based governing equation for reactive transport at equilibrium assumptions is given below

$$\frac{\partial \phi^T \rho_T^E z^E}{\partial t} + \mathbf{E}\mathbf{I} = 0.$$

Here ϕ^T is the total porosity of the (non-dissolved) rock which includes the reactive (mineral) and the fluid part, and it is always constant throughout the course of the simulation.

Due to mineral deposition or precipitation, we have a continuous change in reactive porosity of the system which affects the fluid porosity and the permeability of the system. The alpha operator for a chemical reaction system is given as

$$\alpha_i(\omega) = (1 + c_r(p - p_{ref}))\rho_T^E z_i^E, \quad i = 1, \dots, E. \quad (19)$$

Here z^E is a E -element vector whereas ρ_T^E and c_r are scalar quantities. The term ρ_T^E depends on the overall mole-fraction distribution of the components. For simplicity in this study, we assume that the density of all phases are equal and, using the definition of ρ_T^E from [Sriyanong \(2013\)](#), α_i operator can be written as

$$\alpha_i(\omega) = c(p) \sum_{c=1}^C \sum_{e=1}^E e_{ec} z_c^E z_i^E, \quad i = 1, \dots, E. \quad (20)$$

Space dependent parameter a is modified to include the total porosity instead of fluid porosity. The total porosity is constant throughout the course of the simulation, unlike the fluid porosity which changes as the reaction proceeds. As a result of considering total porosity in the accumulation term, ϕ_o^T becomes a space-dependent parameter instead of state-dependent parameter reducing the non-linearity in the alpha operator

$$a(\xi) = v(\xi)\phi_o^T(\xi). \quad (21)$$

Here ϕ_o^T here stands for the total initial porosity which does not vary with time but only in space. The concept of total porosity and how it depends on the mineral mole fraction is described in details by [Kala](#)

and Voskov (2018). The convection β_i operators are generated by pre-multiplying the Equilibrium Rate Annihilation matrix to the conventional flux terms which factors all components associated with a particular element and yields element flux. The analytic relation for the β_i operators is given below

$$\beta_i(\omega) = \mathbf{E}_{E \times C} \mathbf{I}_{C \times 1}, \quad (22)$$

where $\mathbf{E}$ is the equilibrium annihilation matrix and $\mathbf{I}$ is the flux term. The above equation can be written in terms of phase compositions as

$$\beta_i(\omega) = \sum_{c=1}^C (e_{ic} \sum_{j=1}^P x_{cj} \rho_j \frac{k_{rj}}{\mu_j}), \quad i = 1, \dots, E. \quad (23)$$

where e_{ic} is the amount of element i in component c . These adaptive operators linearize the reactive governing equation and the complete coupled system is solved fully implicitly.

Figure 1—Element and component profile

Numerical simulation results

Next, we show several simulation results for multiphase flow with the dissolution/precipitation reactions.

Reactive flow and transport in 1D

We first describe a simple 1D case which has 1 gas injector and 1 producer in a water-filled aquifer. The parameters for simulation are given in Appendix A and the simulation run times is 1000 days. Only one halite dissolution/precipitation equilibrium reaction is taken into account and the porosity is therefore the function of only one mineral mole fraction. Multiple equilibrium reactions using this framework was simulated in earlier work refer to Kala and Voskov (2018).

Fig. 1 shows the element mole fraction profile on the left and overall component mole fraction profile along with porosity distribution on the right. It is worth noticing that the amount of ions varies based on the mole fraction of water present which moves along the CO₂ front. We solve the primary nonlinear governing equations only for the element mole fractions which is shown in the left figure. Once we have the element mole fraction profile we run the extended flash using the element mole fraction to determine the component mole fractions in the reservoir. As a result, we have a lesser number of nonlinear mass balance equations to solve which makes the system computationally more efficient.

The advantages of this framework are more apparent when multiple reactions are present. In this case, the complete chemical system can be resolved using only few element mole fractions. The right part of Fig. 1

shows the overall composition of the components in which the green line represents the halite mole fraction. Near the injection well, a lot of halite deposition as solid phase can be observed due to vaporization of liquid water from the two-phase mixture. This eventually leads to a decrease in fluid porosity of the system which can be seen by the dashed line in the right figure. This reduction in porosity also affects the permeability of the system the effects of which is the topic of future work.

Multidimensional models

The DARTS framework is also used to mimic the CO_2 storage in saline aquifer. For this application, we used a 9-layer model of Brugge field which is usually used for optimization and history matching research (Peters et al., 2010). Here, we change initial fluids in Brugge field and turn it to a saline aquifer with 1 injection well. The result of simulation after 2500 days of continuous injection is shown in Fig. 2. Here, a composition and porosity profiles are shown for layers 3, 5 and 9. It is clear that layer heterogeneity of Brugge field controls both fluid distribution and following precipitation profile.

Near well mineral precipitation

Here we model near well mineral precipitation scenarios using the DARTS framework. Mineral precipitation is encountered quite often in gas producers and also in CO_2 injectors present in a saline aquifer. To model this process, we create an unstructured homogeneous model with a single well in the center (production or injection depending on the process), see Fig. 3. In this test case, we discretized a radial model with a high-resolution grid with around 8000 control volumes. We use DARTS to simulate both production and injection scenarios in this model.

Figure 2—Component distribution in the Brugges field at $T = 2500$ days a) CO_2 b) $NaCl$ c) porosity

Figure 3—Fine unstructured grid layout

Production well scenario. Gas production often faces the problem of increased well skin-factor overtime due to deposition of mineral species in the near wellbore region. In this simulation example, we employ typical conditions common for North Sea reservoirs as shown in Nair (2015). In these conditions, the connate water in gas reservoirs evaporates over time due to depleted pressure conditions near the producers. This leads to deposition in the near wellbore region, usually at a certain distance away from the well where the boundary of the two-phase region is located.

Figure 4—NaCl deposition near producer well with fine grid

From Fig. 4 one can clearly see two regions with high halite deposition: one in the vicinity of the well and another at approximately 35 to 50 m away from well. In this setup, the water is moving from an external boundary towards the well in the two-phase mixture. Close to the well, all water is vaporised due to the phase transition to a single-phase conditions and all minerals dissolved in the water will precipitate. With time, it significantly reduces the porosity and corresponding permeability which leads to a severe reduction in the production rate. The DARTS framework can accurately capture the described phenomena and can be used for production optimization and well treatment studies. Appendix A gives the simulation parameters used for the model.

Injection well scenario. In this study, we replace the producer with an injector to model precipitation in near injector wells when CO_2 is injected into saline aquifers. As the CO_2 front moves ahead, we see deposition of minerals which is most severe near the injectors due to high-pressure drop between the well and the reservoir, as shown in Fig. 5. The initial condition and the reservoir properties for both cases are given in Appendix A.

Figure 5—NaCl deposition near injection well with fine grid

Conclusions

We presented a simulation framework with chemical equilibrium reactions fully coupled with flow and compositional transport. This new nonlinear formulation reduces the component-based governing equations to the element-based mass balance equations written in terms of element mole fractions, which provides an effective coupling between chemical equilibrium reactions, thermodynamic equilibrium and compositional flow and transport. We extend the thermodynamic phase calculation to include the chemical equilibrium reactions into a nonlinear loop and then rigorously test the framework by plotting the phase distribution of the system.

For reactive flow and transport, we use the recently proposed Adaptive Operator-Based Linearization (OBL) technique to solve the nonlinear mass balance equations in a fully-implicit manner. The developed multiphase flash, together with other relations, provides an effective parametrization of operators in governing equations based on the element composition. The reactive-compositional simulation was performed in the adaptive OBL framework based on pressure and element mole fractions. This choice significantly improves the run-time of simulation due to a reduction in the size of the algebraic system and optimized utilization of the reactive multiphase flash.

Simple mineral dissolution and precipitation model with one equilibrium reaction is simulated in multidimensional models using this approach. To demonstrate the applicability of the developed framework to realistic problems, we model near well precipitation production and injection well scenarios as shown in the last section. We demonstrate that Delft Advanced Research Terra Simulator (DARTS) can be effectively used for the research study of mineral deposition and precipitation in the near-well region. There are ongoing benchmark studies validating DARTS framework against experimental results and other simulation techniques. In future research, the framework will be further extended to include chemical kinetics and permeability alteration to model practical field applications.

Acknowledgements

We acknowledge the financial support from the SRP-NUPUS consortium and thank the research group at the Department of Hydromechanics and Hydrosystem modeling, University of Stuttgart. We would also thank Mark Khait (TU Delft) for his valuable contribution in OBL implementation, Alireza Iranshahr (Shell) for his help with the negative flash, and Stephan de Hoop (TU Delft) for his valuable suggestions.

References

- Acs, G., Doleschall, S., and Farkas, E. (1985). General purpose compositional model. *SPE Journal*, **25** (04): 543–553. SPE-10515-PA.
- Coats, K. (1980). An equation of state compositional model. *SPE Journal*, SPE 8284.
- Collins, D., Nghiem, L., Li, Y.-K., and Grabonstotter, J. (1992). An efficient approach to adaptive-implicit compositional simulation with an equation of state. *SPE Journal*, 15133-PA.

- DARTS (2019). Delft Advanced Research Terra Simulator. In <https://darts-web.github.io/darts-web/>.
- Fan, Y. (2010). Chemical reaction modeling in a subsurface flow simulator with application to in-situ upgrading and CO₂ mineralization phd thesis stanford university. *SPE*, **3**: 1–2.
- Farshidi, S., Fan, Y., Durlofsky, L., and Tchelepi, H. A. (2013). Chemical reaction modeling in a compositional reservoir simulation framework. *SPE Journal*. SPE-163677.
- Garipov, T., Tomin, P., Rin, R., Voskov, D., and Tchelepi, H. (2018). Unified thermo-compositional-mechanical framework for reservoir simulation. *Computational Geosciences*, **22** (4): 1039–1057.
- Iranshahr, A., Voskov, D., and Tchelepi, H. (2010). Generalized negative flash method for multiphase multicomponent systems. *Fluid Phase Equilibria*, **299**: 272–283.
- Iranshahr, A., Voskov, D., and Tchelepi, H. (2013). Tie-simplex based compositional space parameterization: Continuity and generalization to multiphase systems. *AIChE Journal*, **59** (5): 1684–1701.
- Kala, K. and Voskov, D. V. (2018). Parameterization of element balance formulation in reactive compositional flow and transport. ECMOR XVI - 16th European Conference on the Mathematics of Oil Recovery.
- Khait, M. and Voskov, D. (2018a). Operator-based linearization for efficient modeling of geothermal processes. *Geothermics*, **74**: 7–18.
- Khait, M. and Voskov, D. V. (2017). Operator-based linearization for general purpose reservoir simulation. *Journal of Petroleum Science and Engineering*, **157**: 990–998.
- Khait, M. and Voskov, D. V. (2018b). Adaptive parameterization for solving of thermal/compositional nonlinear flow and transport with buoyancy. *SPE Journal*, 182685.
- Lake, L. (1989). *Enhanced Oil Recovery*. Prentice Hall.
- Li, Y.-K. and Nghiem, L. X. (1982). The development of a general phase envelope construction algorithm for reservoir fluid studies. *SPE Journal*. SPE-11198.
- Lichtner, P., Steefel, C., and Oelkers, E. (1996). *Reactive transport in porous media*. Reviews in mineralogy. Mineralogical Society of America.
- Lichtner, P. C. (1985). Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems. *Geochimica et Cosmochimica Acta*, **49** (3): 779–800.
- Lucia, A., Henley, H., and Thomas, E. (2015). Multiphase equilibrium flash with salt precipitation in systems with multiple salts. *Chemical Engineering Research and Design*, **93**: 662–674.
- Michelsen, M. L. (1982). The isothermal flash problem. part I stability. *Fluid Phase Equilibria*, **9**: 1–9.
- Nair, R. (2015). *Near wellbore salt precipitation in gas reservoirs*. MSc Thesis, Department of Geoscience and Engineering, TU Delft.
- Nghiem, L. X., Shrivastava, V. K., Kohse, B. F., and Tripathi, V. (2011). Modeling aqueous phase behavior and chemical reactions in compositional simulation. *SPE Journal*, 141417-MS.
- Peng, D.-Y. and Robinson, D. B. (1976). A new two-constant Equation of State. *Industrial & Engineering Chemistry Fundamentals*, **15** (1): 59–64.
- Peters, E., Arts, R., Brouwer, G., Geel, C., Cullick, S., Lorentzen, R., Chen, Y., Dunlop, K., Vossepoel, E., Xu, R., Sarma, P., Alhuthali, A., and Reynolds, A. (2010). Results of the Brugge benchmark study for flooding optimization and history matching. *SPE Reservoir Evaluation and Engineering*, **13** (3): 391–405.
- Rachford, H. and Rice, J. (1952). Procedure for use of electronic digital computers in calculating flash vaporization at hydrocarbon equilibrium. *Petroleum Transactions AIME Vol.152* (1952) 327–328, 152: 327–328.
- Sriyanong, P. (2013). *Element based formulations for coupled flow, transport and chemical reactions*. MSc Thesis, Department of Energy Resources Engineering, Stanford University.
- Voskov, D. V. (2017). Operator-based linearization approach for modeling of multiphase multi-component flow in porous media. *Journal of Computational Physics*, **337**: 275–288.
- Voskov, D. V., Henley, H., and Lucia, A. (2017). Fully compositional multi-scale reservoir simulation of various CO₂ sequestration mechanisms. *Computers and Chemical Engineering*, **96**: 183–195.
- Voskov, D. V. and Tchelepi, H. A. (2012). Comparison of nonlinear formulations for two-phase multi-component eos based simulation. *Journal of Petroleum Science and Engineering*, 82–83: 101–111.
- Whitson, C. H. and Michelsen, M. L. (1989). The negative flash. *Fluid Phase Equilibria*, **53**: 51–71.
- Yeh, G. and Tripathi, V. (1989). A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resources Research*, **25** (1): 93–108.
- Zaydullin, R., Voskov, D. V., and Tchelepi, H. A. (2017). Comparison of eos-based and k-values-based methods for three-phase thermal simulation. *Transport in Porous Media*, **116** (2): 663–686.

Appendix A:

Simulation parameters

In this section, we describe the fluid and rock properties as well as numerical parameters of OBL used in the simulation. Table (1) shows the rock and fluid properties. The rock is considered low compressible and the total mineral + fluid porosity is taken as 0.3.

Table 1—Rock and fluid properties

Phase	Water	Gas	Solid
Residual saturation (S_r)	0.0	0.0	0.0
End point relative permeability (K_{rje})	1.0	1.0	0.0
Saturation exponent (n_i)	2.0	2.0	-
Viscosity, cP (μ_i)	0.5	0.1	-
Rock compressibility, 1/bar		10^{-7}	
Total porosity		0.3	

Table (2) shows the initial pressure condition of the reservoir and the OBL parameters which are used for adaptive simulation.

Table 2—OBL parameters

Parameter	min	max
Pressure limit	119	131
Composition limit	0	1
Pressure points	2	
Composition points	64	
Initial pressure (P_{in}), bar	125	
Initial pressure (P_{inj}), bar	130	

Table (3) shows the initial and injection reservoir mole fractions.

Table 3—Reservoir compositions

Elements	H_2O	CO_2O	Na^+	Cl^-
initial	0.69	0.01	0.15	0.15
injection	0.01	0.98	0.005	0.005

Table (4) shows the thermodynamic partition coefficient and the chemical equilibrium constants for equilibrium reactions.

Table 4—Thermodynamic and chemical properties

Elements	H_2O	CO_2O	$NaCl$
K	0.1	2.5	
K_{sp}	-	-	36

Compressible Fluid Case

Below, we provide the pressure-based K values which are used in the Darts simulation in the near well precipitation case under isothermal conditions of 373 K.

Table 5—Thermodynamic and chemical properties for compressible case

Pressure(bar)	50	60	70	80	90	100	110	120	130	140
H_2O	0.1080	0.0945	0.0849	0.0779	0.0726	0.0684	0.0651	0.0624	0.0602	0.0584
CH_4	1149.0	972.0	845.0	750.0	676.0	617.0	569.0	528.0	494.0	465.0

Table (6) shows the OBL parameters which are used for adaptive simulation.

Table 6—OBL parameters near well precipitation

Parameter	min	max
Pressure limit	50	140
Composition limit	0	1
Pressure points		16
Composition points		64

The pressure based K values are same as given in table (5).

Production well

Below the tables provide the reservoir and fluid properties used in minearl precipitation scenario. Only the properties which are different from the 1D case are defined.

Table 7—Rock and fluid properties for DARTS

Phase	Water	Gas	Solid
Density (ρ) kg/m^3	1000	50	2000
Initial pressure, bar		135	
Production Pressure, bar		55	
Total porosity		0.2	
Number of grid blocks		385	

Below the table shows the initial condition of the reservoir in the single production well scenario.

Table 8—Reservoir compositions for production well scenario

Elements	H_2O	CH_4	Na^+	Cl^-
initial	0.2	0.7	0.05	0.05

Injection well

Below the table shows the initial and injection condition of the reservoir in the single injection well scenario. The missing properties are similar to production well case.

Table 9—Rock and fluid properties for injection well scenario

Initial pressure, bar	105
Injection Pressure, bar	135
Total porosity	0.2
Number of grid blocks	7687

Table 10—Reservoir compositions injection well scenario

Elements	H_2O	CH_4	Na^+	Cl^-
initial	0.90	0.01	0.045	0.045
injection	0.0	1.0	0.0	0.0

Appendix B:

Convergence study

Here we show the convergence study for halite precipitation simulation. The different grid sizes used for the simulation are shown below, where Grid A has the highest resolution and Grid D the lowest resolution.

Figure 6—Convergence Study with grid blocks a) 11111 b) 1786 c) 1005 d) 643

The parameters used for this convergence study are similar to the ones used for running the mineral precipitation case which can be found in Appendix A. Fig. 7 shows the results of the NaCl mineral precipitation at $T = 3000$ days for different grid resolution cases. We plot the mole fraction value of each grid block with respect to distance in the reservoir. Since we have radial coordinates with a maximum radius of 100 m we represent this 2D system in a 1D displacement scenario to find the deposition zone. In Fig. 7 a) NaCl mole fraction in each grid block is plotted as a function of distance to the production well. In Fig. 7 b), all the control volume mole fractions are plotted in one figure. This representation gives us a clear idea of the estimated zone of mineral deposition for this case. From figures, one can see that grid A with the highest resolution has a sharp increase in halite mole fraction in the deposition zone and almost overlap with the resolution in grid B. These results demonstrate the DARTS framework's ability to accurately capture mineral deposition in realistic models.

(a) Mole fraction profile for individual grid resolutions

(b) Concentration profile for all grid resolution combined

Figure 7—Halite mole fraction vs distance