ELEMENT-BASED FORMULATIONS FOR COUPLED FLOW, TRANSPORT, AND CHEMICAL REACTIONS

A REPORT
SUBMITTED TO THE DEPARTMENT OF ENERGY
RESOURCES ENGINEERING
OF STANFORD UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

Pasawich Sriyanong
June 2013

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and quality, as partial fulfillment of the degree of Master of Science in Petroleum Engineering.

(Hamdi Tchelepi) Principal Adviser

Abstract

A numerical modeling of coupled flow, transport, and chemical reactions is critical to understand the dynamic processes in natural porous media and manage subsurface resources, such as CO_2 sequestration, water aquifers, and oil reservoirs. In this work, two molar formulations for coupled flow, transport, and chemical reactions are proposed, namely, the overall-composition and the element formulations. Both formulations assume an element-based statement of the governing equations, which are composed of the element mass-conservation equations, chemical reactions, phase-equilibrium, and constraint relations. A general treatment of the solid phase is employed, and the formulations allow for any component to exist in any phase. In the two proposed formulations, the primary equations set is composed of the element conservation equations and the kinetic reactions. The overall fraction for an element is introduced in the element formulation and used as a primary variable. The standard low-order finite-volume, fully-implicit method, which is widely used in reservoir simulation, is the basis for discretizing the equations. In the new formulations, variable substitution due to phase appearance, or disappearance, is not required; however, the equilibrium relations are treated separately from the mass conservation equations and solved using exact flash calculations. The element formulation is demonstrated using a simple model problem, which describes one-dimensional CO_2 injection into water containing $NaCl$ salt, and with only one equilibrium precipitation-dissolution reaction involving $NaCl$ salt. A two-step phase-behavior computation procedure is developed for the model problem. The results are numerically identical whether a component is allowed to be completely absent from a phase, or if a trace concentration is used. We also show that the phase behavior can be resolved from any starting fractions of elements, or overall compositions.

Acknowledgements

First and foremost, I would like to express my sincere gratitude to my advisors, Prof. Hamdi Tchelepi and Dr. Denis Voskov, for their time, guidance, and motivation in this research. Prof. Hamdi Tchelepi gave me freedom to explore and experiment in many research areas. I learned many things from several discussions with him, both about research work and about life in general. I would like to thank him for his great patience and understanding when I got lost, and things did not work out as expected. Dr. Denis Voskov helped me shape the scope of this work, and provided a lot of insightful comments. I always came out of his office with hope and direction to move forward. His help with my understanding of AD-GPRS is also highly appreciated.

There are a few people inside and outside of the Department of Energy Resources Engineering whom I would like to particularly acknowledge. I would like to thank Rustem Zaydullin for his help with flash calculations and modifying AD-GPRS. I would like to thank Sara Farshidi for very helpful discussions about reactive transport modeling and about the implementation of coupled reactions in GPRS. I would also like to thank Prof. Marc Hesse from Jackson School of Geosciences, the University of Texas at Austin, for his help with my other research work on the anomalous transport simulation, though it is not included as a part of this thesis. Special thanks go to Prof. Anthony Kovscek, my undergraduate advisor, for leading me to the world of research in the department.

This work would not be possible without the financial support from the industrial affiliates of SUPRI-B (Reservoir simulation) research group and PI/ADNOC (Petroleum Institute/Abu Dhabi National Oil Company). They are greatly acknowledged.

All my friends in the Department of Energy Resources Engineering as well as in other departments are an important part of my life. I would like to thank them for their support through both up and down moments at Stanford.

Most importantly, I am forever indebted to my parents for their unwavering love, support, and inspiration.

Contents

List of Tables

List of Figures

Chapter 1

Introduction and Literature Review

Subsurface processes are very complex. Geological processes that have occurred over millions of years shape the large-scale subsurface characteristics, such as reservoir geometry, orientation, and structures (faults, fractures, seals, etc.), as well as small-scale characteristics, such as anisotropy and heterogeneity. Dynamic processes of interest, e.g., hydrocarbon recovery, CO_2 sequestration, and subsurface water management, are also governed by complex interactions of various physical phenomena, which are tightly coupled and occur at multiple spatial and time scales. Numerical modeling has become an essential tool in managing subsurface resources, since it helps to enhance the understanding of the complex subsurface processes, integrate available information, and make forecasts.

The development of theoretical and numerical tools for simulating subsurface problems has been important in both the reservoir engineering and hydrogeology communities. The reservoir engineering community often deals with problems involving complicated phase behavior and the transport of multiple components in multiple fluid phases. Such problems include steam, or gas, injection and other EOR processes

[1]. Complicated Equation-of-State (EOS) compositional models are often required in reservoir simulation. Emphasis is on ensuring robustness and efficiency in simulating the coupling between the thermodynamic phase equilibrium and the nonlinear transport of multiple components [2–5]. Traditionally, chemical reactions are not treated as having a first-order impact on the models. Recently, chemical reaction models have been incorporated in reservoir simulation frameworks for some specific purposes [6–8].

On the other hand, the hydrogeology community has been dealing with subsurface modeling of multiple components and multiple chemical reactions. There are a few pioneering works that have influenced the development of several reactive transport modeling tools. The initial work by Lichtner [9] laid the foundational theory of continuum models for mass transport and chemical reactions. Yeh and Tripathi [10, 11] compared and evaluated many numerical techniques for simulating solute transport, and they presented both theoretical and numerical frameworks for reactive transport. Later, Steefel and Lasaga [12] extended reactive transport modeling to non-isothermal, kinetically-controlled, aqueous-solid interactions. Current reactive transport models can incorporate a wide variety of complicated chemical reactions, including surface complexation, dissolution-precipitation, adsorption-desorption, and redox reactions [13]. The emphasis has, however, been on the aqueous phase. Water is often assumed to be the prevalent component in the aqueous phase. Various assumptions are made to simplify the properties of the gas phase and Non-Aqueous Phase Liquids (NAPLs) and the partitioning of components across the fluid phases. Reactive transport modeling in subsurface hydrogeology has not emphasized equilibrium phase behavior of hydrocarbon mixtures that can form multiple phases.

Due to emerging interest in complicated subsurface dynamic processes like CO_2 sequestration, methane hydrate recovery, and unconventional reservoirs, there is a growing need in integrating full chemical reaction modeling capabilities with compositional reservoir simulation [14]. Combining chemical reactions with full phase-equilibrium EOS models is required for accurate representation of these processes. Coming up with a numerical model that performs such integration is challenging in many aspects. The model must be able to handle realistic systems that consist of large number of components, multiple phases, and several chemical reactions. Moreover, complex nonlinear interactions are not well understood. These include the effect of reactive components on phase equilibrium, how to scale reactive transport processes from pore scale to field scale, and the effects of dissolution and precipitation on large-scale flow and transport [13].

The main objective of this research effort is to develop a new formulation for fully-coupled flow, transport, and chemical reactions.

1.1 Governing equations

The governing equations that describe coupled flow, transport, and chemical reactions for isothermal systems consist of component mass-conservation equations, phase-equilibrium, and constraint relations. The form of the equations in this section is adapted from [1] and [15].

1.1.1 Component conservation equations

A system of n_c components is considered. The word "component" here refers to the definition commonly used in the reservoir engineering community, and it is equivalent to the label "species" in the hydrogeology community. Each component can exist in one solid phase and up to n_p^f fluid phases. The n_c component conservation equations can be written as [1]:

$$\frac{\partial N_c}{\partial t} + L_c = \sum_{k=1}^{n_k} v_{ck} r_k + \sum_{q=1}^{n_q} v_{cq} r_q \qquad (c = 1, \ldots, n_c), \tag{1.1.1}$$

where N_c is the total mass of component c, and L_c is the flow term. v_{ck} is the stoichiometric coefficient of component c in kinetic reaction k, v_{cq} is the stoichiometric coefficient of component c in equilibrium reaction q. Here, r_k is the reaction rate of kinetic reaction k, and r_q is the reaction rate of equilibrium reaction q. n_k and n_q are, respectively, the number of kinetic and equilibrium reactions, so that $n_r = n_k + n_q$.

$$N_c = \sum_{p=1}^{n_p^f} (\phi \rho_p S_p X_{cp}) + \rho_s (1 - \phi) X_{cs} \qquad (c = 1, \ldots, n_c), \tag{1.1.2}$$

where ϕ is porosity, ρ_p is phase density, S_p is phase saturation, X_{cp} is phase composition, ρ_s is solid phase density, and X_{cs} is solid phase composition. Reactions that involve solids can change the pore volume that is available for flow. Using this definition for N_c, the change in the pore volume can be accounted for by modeling porosity change.

The flow term, L_c, includes advective and dispersive fluxes, and a well term:

$$L_c = \nabla \cdot \sum_{p=1}^{n_p^f} (\rho_p X_{cp} \mathbf{u}_p - \rho_p \phi S_p \mathbf{D}_{cp} \nabla X_{cp}) + q_c^W \quad (c = 1, \ldots, n_c)\,, \tag{1.1.3}$$

where $\mathbf{u}_p$ is the Darcy velocity of fluid phase p, $\mathbf{D}_{cp}$ is the dispersion tensor for component c in phase p, and q_c^W is the well rate of component c. Instead of the full Navier-Stokes conservation of momentum, Darcy's law is used to represent the velocity field. The Darcy velocity is written as:

$$\mathbf{u}_p = -\mathbf{K}\frac{k_{rp}}{\mu_p}\left(\nabla P - \rho_p g \nabla D\right) \qquad \left(p = 1, \ldots, n_p^f\right), \tag{1.1.4}$$

where $\mathbf{K}$ is the permeability tensor, k_{rp} is the relative permeability for fluid phase p, μ_p is the viscosity of fluid phase p, P is the pressure, g is the gravitational acceleration, and D is depth. The pressure gradient is given by ∇P, since capillary pressure is neglected. So, the pressure of any fluid phase p, P_p, is equal to P. If capillary pressure is retained, the only place that P_p shows up is in the pressure gradient term, which becomes ∇P_p. The capillary pressure relation is given by:

$$P_i - P_j = P_{ij}^C, \qquad \text{fluid phase } \forall\, i \neq j \in \{1, \ldots, n_p^f\}, \tag{1.1.5}$$

where P_{ij}^C is the capillary pressure between phases i and j, which is a function of phase saturations only.

The component conservation equations (Equation 1.1.1) can be written in a more concise format as:

$$\frac{\partial \mathbf{N}}{\partial t} + \mathbf{L} = \mathbf{V}\mathbf{r}, \tag{1.1.6}$$

where $\mathbf{N} = (N_1, \ldots, N_{n_c})^T$, $\mathbf{L} = (L_1, \ldots, L_{n_c})^T$, $\mathbf{V}$ is the stoichiometric matrix, and $\mathbf{r} = (\mathbf{r_k}, \mathbf{r_q})^T = (r_1, \ldots, r_{n_k}, r_{n_k+1}, \ldots, r_{n_k+n_q})^T$.

1.1.2 Phase-equilibrium and constraint relations

There are $n_c n_p^f$ phase-equilibrium relations, n_p^f linearly independent phase-composition constraints (see [5]), and one saturation constraint. These relations can be written as:

$$\text{Phase-equilibrium:} \qquad f_{ci} = f_{cj} \quad \left(\forall\, c \,\&\, \forall\, i \neq j \in \{s, 1, \ldots, n_p^f\}\right), \tag{1.1.7a}$$

$$\text{Composition constraints:} \quad \sum_{c=1}^{n_c} X_{cp} = 1 \qquad \left(p = 1, \ldots, n_p^f\right), \tag{1.1.7b}$$

$$\text{Saturation constraints:} \quad \sum_{p=1}^{n_p^f} S_p = 1, \tag{1.1.7c}$$

Here, f_{ci} is the fugacity of component c in phase i.

1.1.3 Natural-variables set

The natural-variables set, $\mathbf{Y}$, contains one pressure, P, n_p^f phase saturations, S_p, $n_c n_p^f$ fluid phase compositions, X_{cp}, and n_c solid phase composition, X_{cs}:

$$\mathbf{Y} = (P, S_p, X_{cp}, X_{cs}) \qquad \left(c = 1, \ldots, n_c \,\&\, p = 1, \ldots, n_p^f\right). \tag{1.1.8}$$

The total number of variables is $n_c n_p^f + n_p^f + n_c + 1$. Other variables are functions of $\mathbf{Y}$ only. The component conservation equations (Equation 1.1.6) and the phase-equilibrium and constraint relations (Equation 1.1.7) are used to close the system. The total number of equations is $n_c n_p^f + n_p^f + n_c + 1$. The number of variables is, therefore, equal to the number of independent equations.

1.1.4 Simplified governing equations

Up to this point, a component is allowed to exist in any phase. If chemistry dictates that some components exist only in either fluid or solid phases, distinctions between the fluid and solid components can be made. The component conservation equations (Equation 1.1.1) can then be simplified to [1]:

$$\frac{\partial N_c}{\partial t} + L_c = \sum_{k=1}^{n_k} v_{ck} r_k + \sum_{q=1}^{n_q} v_{cq} r_q \qquad (c = 1, \ldots, n_f)\,, \tag{1.1.9a}$$

$$\frac{\partial C_c}{\partial t} = \sum_{k=1}^{n_k} v_{ck} r_k + \sum_{q=1}^{n_q} v_{cq} r_q \qquad (c = 1, \ldots, n_s)\,, \tag{1.1.9b}$$

where C_c is the solid component concentration. Here, n_f and n_s refer to the number of fluid and solid components, respectively ($n_c = n_f + n_s$). There is no flow term for the solid components. Under this simplification, phase-equilibrium relations exist only for fluid components that partition across multiple fluid phases.

Some fluid components are also often assumed to exist only in a single fluid phase. For example, aqueous ions are assumed to reside only in the aqueous phase. The number of variables and the number of independent equations are still guaranteed to match, since one less phase-equilibrium relation is needed when a component does not exist in a phase.

The simplified component conservation equations (Equation 1.1.9) could still be written concisely as the general component conservation equations (Equation 1.1.6), but with $\mathbf{N} = (N_1, \ldots, N_{n_f}, C_1, \ldots, C_{n_s})^T$ and $\mathbf{L} = \big(L_1, \ldots, L_{n_f}, 0, \ldots, 0\big)^T$.

1.2 Element-based governing equations

The component conservation equations, in general, consist of both slow (kinetic) and fast (equilibrium) reactions. Whether reactions are considered slow, or fast, is relative to the flow, which can be quantified by the Damkohler number [16]. Having a wide range of time scales in the component conservation equations is problematic, however. Very fast reactions causes the component conservation equations to be stiff [17]. To overcome the stiffness, it is necessary to eliminate equilibrium reactions from the conservation equations. There are quite a few approaches to achieve this elimination, such as the primary-species approach [17], which has been used very widely in the hydrogeological community, or the equilibrium-rate annihilation approach [7, 8].

Fan [16] proposed an element-based approach, whereby an element is defined as an atom (e.g., carbon, hydrogen, oxygen), or a compound (e.g., CO_2, H_2O, CO_3^{2-}) that "does not partition into smaller entities by chemical reactions in the system under consideration" [1]. Using this approach, the n_c component conservation equations are transformed into the n_e element conservation equations and the n_r independent chemical-reaction relations. Since the number of components is equal to the number of elements plus the number of independent reactions ($n_c = n_e + n_r$) [1], the system of n_c components can be closed by the (1) element conservation equations, (2) chemical reaction relations, (3) phase-equilibrium, and (4) constraint relations.

1.2.1 Element conservation equations

The n_c component conservation equations (Equation 1.1.6) can be linearly transformed to n_e element conservation equations by multiplying both sides of Equation 1.1.6 with the constant element stoichiometric matrix, $\mathbf{E}$, which is defined as:

$$\mathbf{E}_{n_e \times n_c} = \begin{bmatrix} E_{1,1} & \dots & E_{1,n_c} \\ \vdots & E_{e,c} & \vdots \\ E_{n_e,1} & \dots & E_{n_e,n_c} \end{bmatrix}, \tag{1.2.1}$$

where $E_{e,c}$ is the number of elements e in component c, and n_e refers to the number of elements. So, $\mathbf{E}$ is $n_e \times n_c$.

The element conservation equations are given by:

$$\frac{\partial}{\partial t}\left(\mathbf{E}_{n_e \times n_c}\mathbf{N}\right) + \mathbf{E}_{n_e \times n_c}\mathbf{L} = 0. \tag{1.2.2}$$

Chemical reactions behave like sources, or sinks, for components, but not for elements. The right hand side of Equation 1.2.2 is zero, indicating that the reaction term disappears regardless of whether the reactions are kinetic, or equilibrium.

1.2.2 Chemical-reaction relations

Chemical reaction relations are provided separately from the element conservation equations: one for each independent reaction. Kinetic and equilibrium reactions are also treated differently.

Kinetic reactions

Farshidi et al. [14] showed that it is possible to perform a linear combination of the component conservation equations, so that each kinetic reaction rate appears only once in the n_k reaction relations. The kinetic reaction relations can be written in the concise form as:

$$\frac{\partial}{\partial t}\left(\mathbf{\Psi}_{n_k \times n_c}\mathbf{N}\right) + \mathbf{\Psi}_{n_k \times n_c}\mathbf{L} = \mathbf{r_k}, \tag{1.2.3}$$

where $\mathbf{\Psi}$ is an $n_k \times n_c$ constant "kinetic reaction" matrix that linearly transforms the n_c component conservation equations to n_k kinetic reaction relations. Such a matrix was defined in [14]. Several kinetic rate expressions ($\mathbf{r_k}$), ranging from simple to extremely complicated, have been developed [12, 17, 18]. In order to be used in the kinetic reaction relations (Equation 1.2.3), these expressions have to be written as a function of variables $\mathbf{Y}$.

Equilibrium reactions

In cases that reactions are very fast, the Local Equilibrium Assumption (LEA) can be used. Under this assumption, chemical equilibrium is achieved instantly at every point in space and time, and the reaction rates are not explicitly defined [1]; instead, the state of chemical equilibrium can be described by the mass-action law:

$$Q_q - K_q = \prod_{p=1}^{n_p} \prod_{c=1}^{n_c} \alpha_{cp}^{v_{cq}} - K_q = 0 \qquad (q = 1, \ldots, n_q), \tag{1.2.4}$$

where Q_q and K_q are the activity product and the equilibrium constant of equilibrium reaction q, respectively. In Equation 1.2.4, α_{cp} is the activity of component c in phase p.

1.3 Nonlinear formulations

In the reservoir simulation community, the nonlinear governing equations are typically linearized and solved using Newton's method. Different variable sets can be selected during the linearization process. Several formulations and solution techniques for compositional simulation have been proposed and used [19]. Different widely-used formulations for compositional simulation have been reviewed, and their performance has been evaluated [20, 21]. In this section, two families of nonlinear formulations are discussed, namely, the natural-variables and molar formulations.

It should be noted that the emphasis of this work is on the Finite-Volume (FV) method with the backward-Euler, fully-implicit method (FIM). The stability properties of FIM are very desirable for modeling the tightly-coupling, highly-nonlinear phenomena that arise from coupling phase-equilibrium and chemical reactions. Sequential treatment, which is used in many simulators, including TOUGHREACT, UTCHEM, and GWB, could lead to serious stability problems [14]. The high-resolution FIM solution also serves as a reference solution.

1.3.1 Natural-variables formulation

Coats [4] proposed the natural-variables formulation for compositional displacements without chemical reactions. The natural-variables set corresponds to the variable set **Y** shown in Equation 1.1.8. The primary equations set consists of the conservation equations, and the primary variables are pressure, P, phase saturations, S_p, and a subset of phase compositions, X_{cp}. The natural-variables formulation has arguably been the most widely-used formulation in the reservoir simulation community.

For coupled flow, transport, and reactions model, Fan [1] selected the natural-variables formulation as the starting point in his element-based approach, and he gave two reasons for his choice. The first reason is the efficiency in constructing the Jacobian matrix, since the governing equations are already cast in terms of the natural variables. The second reason is the efficiency in the phase behavior computations.

Variable and equation types

The pressure, P, phase saturations, S_p, and some phase composition, X_{cp} are chosen as the primary variables. The number of phase saturations used as primary variables depends on the phase state of a grid block. The remaining variables in the natural-variables set (Equation 1.1.8) are the secondary variables. The primary equations are the n_e element conservation equations (Equation 1.2.2) and n_k kinetic reaction relations (Equation 1.2.3). The rest, which include phase-equilibrium and constraint relations (Equation 1.2.4) and equilibrium reactions relations (Equation 1.1.7), are the secondary equations. In some special cases, some kinetic reaction relations may be decoupled from the primary equation set, if the kinetic reactions are localized [16]. Table 1.1 summarizes the types of equations and variables in the natural-variables formulation.

Types	**Equations**	**Variables**
Primary	element conservation equations kinetic reaction relations	P some S_p and some X_{cp}
Secondary	equilibrium reaction relations (local kinetic reaction relations) phase-equilibrium and constraints	the rest of X_{cp}

Table 1.1: Summary of types of equations and variables in the natural-variables formulation.

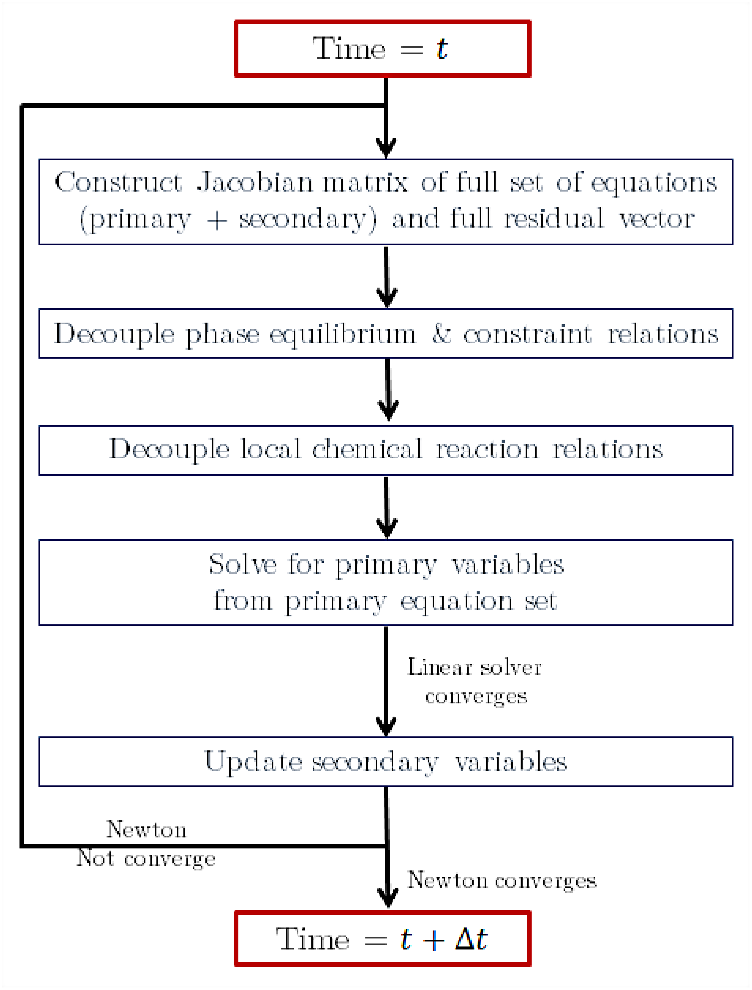


Figure 1.1: Flow chart for the solution procedure of the natural-variables formulation

Solution procedure

For each Newton iteration, the Jacobian matrix of the full set of the element-based governing equations is constructed. This means that the derivatives of all the governing equations with respect to all the variables in the natural-variables set are needed. The residual vector is also built. Second, the secondary equations are decoupled from the primary equations by using a Schur complement. This decoupling process may be done in multiple steps [16]: one for phase-equilibrium and constraint relations, one for equilibrium reaction relations, and one for local kinetic reaction relations. Then, the primary equations are solved for the primary variables. When the linear solver converges, the primary variables are known. Phase-behavior computations are performed for some of the grid blocks to determine the phase state and whether variable substitution is required for the next Newton iteration. The secondary variables are then updated. This solution procedure is summarized in Figure 1.1.

1.3.2 Molar formulation

Many authors have developed molar formulations for compositional simulation when chemical reactions are excluded [21].

Young and Stephenson [5] proposed a molar formulation for compositional flow. The formulation allows for an arbitrary number of n_h components in two hydrocarbon phases and a single component only in the water phase. The molar variable set consists of overall hydrocarbon phase density, water phase density, the fraction of hydrocarbon in the light phase, phase compositions, overall compositions, and pressure. The primary equations are the hydrocarbon phase-equilibrium relations, the component conservation equations, and the saturation constraint. The primary variables are pressure, either overall hydrocarbon phase density, or water phase density, and $n_h - 1$ overall compositions.

Chien et al. [22] proposed a variant of the Young and Stephenson's molar formulation. Instead of having phase compositions in the molar variable set, the phase-equilibrium ratios (K-values) are used.

Acs et al. [23] proposed a volume-balance formulation that uses the extensive molar variables instead of the overall compositions. An additional constraint relation is based on the fact that the fluid volume in a grid block must fill the pore volume.

Unlike the natural-variables formulation, molar formulations for coupled flow, transport, and chemical reactions have not been investigated.

1.4 Thesis Outline

In Chapter 2, two molar formulations for coupled flow, transport, and chemical reactions are proposed, namely, the overall-compositions and the element formulations. Challenges in performing phase behavior computations are discussed. The differences between these formulations and the natural-variables formulation for coupled reactions are highlighted.

In Chapter 3, the overall element formulation is applied on a model problem, which involves CO_2 injection into water containing $NaCl$ salt. The solution procedure for the element formulation is explained in detail. Finally, some results are discussed.

In Chapter 4, the main conclusions are drawn and the possible future extensions of molar formulations for coupled reactions are presented.

Chapter 2

Molar Formulations for Coupled Reactions

2.1 Overall-composition formulation

2.1.1 Element-based governing equations

A system of n_c components is considered. Each component can exist in any of the n_p phases. n_p^f fluid phases and n_p^s solid phases are assumed, so that the total number of phases is $n_p = n_p^f + n_p^s$. Note that multiple solid phases may be present. n_p^s is equal to one, if the solid phase is treated as the ensemble of all the solids. One can also let n_p^s be equal to the number of minerals, if each mineral is treated as a separate solid phase. An alternative form of N_c is proposed, which is given by:

$$N_c = \sum_{p=1}^{n_p} \hat{\phi} \rho_p S_p X_{cp} \qquad (c = 1, \ldots, n_c) \,, \tag{2.1.1}$$

where $\hat{\phi}$ represents the reactive porosity, ρ_p is the phase density, S_p is the phase saturations, and X_{cp} is the phase composition. N_c here is different from that in Equation 1.1.2. Under the definition in Equation 2.1.1, the porosity, $\hat{\phi}$, includes the volume occupied by the solids that do not participate in chemical reactions. Here, unit porosity indicates that all the solids can be involved in chemical reactions. The saturation (relative amount) of a solid can change due to precipitation-dissolution reactions, while $\hat{\phi}$ does not. Keeping track of the pore-volume open to flow is straightforward due to this general treatment of the solid phase. The relative permeabilities of the fluid phases must be defined carefully as both solids and fluids may be present in the pore space. Note that $\hat{\phi}$ is related to ϕ defined in Chapter 1 by the following relation:

$$\phi = \left(1 - \sum_{p=1}^{n_p^s} S_p \right) \hat{\phi}. \tag{2.1.2}$$

The component mass-conservation equations (Equation 1.1.1) can be reformulated in terms of overall-composition variables as follows:

$$\frac{\partial}{\partial t} \left(\hat{\phi} \rho_T z_c \right) + L_c = \sum_{k=1}^{n_k} v_{c,k} r_k + \sum_{q=1}^{n_q} v_{c,q} r_q \qquad (c = 1, \ldots, n_c), \tag{2.1.3}$$

Here, ρ_T is the total overall component density, and z_c is the overall-composition fraction. L_c is defined in the same way as Equation 1.1.3. Note that the total component mass, N_c, from Equation 2.1.1 is used instead of the one from Equation 1.1.2.

The total component density, ρ_T, can be written as:

$$\rho_T = \sum_{p=1}^{n_p} \rho_p S_p = \frac{1}{\sum_{p=1}^{n_p} \frac{\nu_p}{\rho_p}}. \tag{2.1.4}$$

The overall-composition fraction, z_c, is then expressed as:

$$z_c = \frac{\sum_{p=1}^{n_p} \rho_p S_p X_{cp}}{\sum_{p=1}^{n_p} \rho_p S_p} = \sum_{p=1}^{n_p} \nu_p X_{cp}, \tag{2.1.5}$$

where ν_p in Equations 2.1.4 and 2.1.5 is the phase molar fraction, which is given by:

$$\nu_j = \frac{\rho_j S_j}{\sum_{p=1}^{n_p} \rho_p S_p}. \tag{2.1.6}$$

The phase saturation, S_p, can be written as a function of ν_p as follows:

$$S_p = \frac{\dfrac{\nu_p}{\rho_p}}{\sum_{p=1}^{n_p} \dfrac{\nu_j}{\rho_j}}. \tag{2.1.7}$$

Here, ρ_T, z_c, and S_p are written as functions of ν_p. Note that ν_p is used in the phase behavior computation of molar formulations [19].

Equation 2.1.3 can be rewritten in the following compact form:

$$\frac{\partial}{\partial t}\left(\hat{\phi}\rho_T \mathbf{z_c}\right) + \mathbf{L} = \mathbf{Vr}, \tag{2.1.8}$$

where $\mathbf{z_c} = (z_1, z_2, \ldots, z_{n_c})^T$, $\mathbf{L} = (L_1, L_2, \ldots, L_{n_c})^T$, and $\mathbf{r} = (r_1, r_2, \ldots, r_{n_r})^T$.

The n_c component conservation equations (Equation 2.1.8) are then transformed into n_e element conservation equations by multiplying both sides of Equation 2.1.8

by the element stoichiometric matrix, $\mathbf{E}_{n_e \times n_c}$, so that

$$\frac{\partial}{\partial t}\left(\hat{\phi}\rho_T \mathbf{E}\mathbf{z_c}\right) + \mathbf{E}\mathbf{L} = 0. \tag{2.1.9}$$

This is a system of n_e element conservation equations in terms of overall-composition variables. As noted in the previous chapter, reaction terms do not appear in the element balances.

The kinetic reaction matrix, $\boldsymbol{\Psi}_{n_k \times n_c}$, is used to transform the component conservation equations (Equation 2.1.8) into n_k kinetic reaction relations:

$$\frac{\partial}{\partial t}\left(\hat{\phi}\rho_T \boldsymbol{\Psi}\mathbf{z_c}\right) + \boldsymbol{\Psi}\mathbf{L} = \mathbf{r_k}. \tag{2.1.10}$$

For equilibrium reactions, the mass-action law of Equation 1.2.4 is still applicable, and it is repeated here for convenience:

$$Q_q - K_q = \prod_{p=1}^{n_p}\prod_{c=1}^{n_c} \alpha_{cp}^{v_{cq}} - K_q = 0 \qquad (q = 1, \ldots, n_q). \tag{2.1.11}$$

The phase-equilibrium and constraint relations are summarized in Table 2.1.

Phase-equilibrium	$f_{ci} = f_{cj}$	$(\forall\, c\,\&\,\forall\, i \neq j \in \{1, \ldots, n_p\})$
Overall mole fraction constraints	$z_c = \sum_{p=1}^{n_p} \nu_p X_{cp}$	$(c = 1, \ldots, n_c)$
Phase molar constraints	$\sum_{c=1}^{n_c} (X_{ci} - X_{cj}) = 0$	$(\forall\, i \neq j \in \{1, \ldots, n_p\})$
Molar phase fraction constraints	$\sum_{p=1}^{n_p} \nu_p = 1$	
Overall composition constraints	$\sum_{c=1}^{n_c} z_c = 1$	

Table 2.1: Summary of phase equilibrium and constraint relations

Note that an overall-composition formulation can still be developed, if the definition of N_c in Equation 1.1.2 is used instead of the one in Equation 2.1.1. An overall-composition formulation can also be developed from the simplified component conservation equations (Equation 1.1.9). However, ρ_T and z_c will not be in the familiar forms of Equations 2.1.4 and 2.1.5.

2.1.2 Molar variable set

In the overall-composition formulation, the following variable set is used:

$$\mathbf{\Upsilon_c} = (P, z_c, \nu_p, X_{cp}) \qquad (c = 1, \ldots, n_c \; \& \; p = 1, \ldots, n_p)\,. \tag{2.1.12}$$

Other properties are functions of $\mathbf{\Upsilon_c}$. The total number of variables is $n_c n_p + n_c + n_p + 1$. The system is closed by the n_e element conservation equations (Equation 2.1.9), the n_r independent reaction relations (Equations 2.1.10 and 2.1.11), and the $n_c n_p + n_p + 1$ phase-equilibrium and constraint relations (Equation 3.2.1). The total is $n_c n_p + n_c + n_p + 1$ equations ($n_c = n_e + n_r$). The number of variables is equal to the number of governing equations in this overall-composition formulation.

2.1.3 Solution strategies

Variable and equation types

The pressure, P, and overall compositions, z_c for $c = 1, \ldots, n_e + n_k - 1$, are chosen as the primary variables, which are denoted as $\mathbf{\Upsilon_c^P}$. The rest of the variables are the secondary variables, which are denoted as $\mathbf{\Upsilon_c^S}$. It has not been investigated which z_c's are more appropriate to be used as primary variables. Efforts should be directed toward establishing a method to select z_c's as primary variables based on component molar masses, chemical reactions, and phase equilibrium for a given coupled reaction system.

The primary equations are the n_e element conservation equations (Equation 2.1.9) and n_k kinetic reaction relations (Equation 2.1.10). The rest of the equations, which include equilibrium reaction relations, phase equilibrium, and constraint relations, are secondary equations. Note that the secondary equations are local. Table 2.2 summarizes the types of equations and variables in the overall-composition formulation.

Types	**Equations**	**Variables**
Primary	element conservation equations	P
	kinetic reaction relations	z_c for $c = 1, \ldots, n_e + n_k - 1$
Secondary	equilibrium reaction relations	z_c for $c = n_e + n_k, \ldots, n_c$
	phase equilibrium and constraints	ν_p, X_{cp}

Table 2.2: Summary of types of equations and variables in the overall-composition formulation.

Solution procedure

The overall-composition formulation is a member of the molar formulations family. The solution procedure is different from the one used for the natural-variables formulations described in Chapter 1. The solution procedure for molar formulations implemented in AD-GPRS [21, 24] is extended to account for chemical reactions. First, for each Newton iteration, for the given P and $n_e + n_k - 1$ z_c's, the secondary equation set is solved for the secondary variables. The secondary equation set, which is denoted by $\mathbf{F}$, is written as:

$$F_k = f_{ci} - f_{cj} = 0, \qquad (\forall\, c \,\&\, \forall\, i \neq j \in \{1, \ldots, n_p\}) \tag{2.1.13a}$$

$$F_{k+n_c(n_p-1)} = z_c - \sum_{p=1}^{n_p} \nu_p X_{cp} = 0, \qquad (c = 1, \ldots, n_c) \tag{2.1.13b}$$

$$F_{k+n_c n_p} = \sum_{c=1}^{n_c} (X_{ci} - X_{cj}) = 0, \qquad (\forall\, i \neq j \in \{1, \ldots, n_p\}) \tag{2.1.13c}$$

$$F_{n_c n_p + n_p} = \sum_{p=1}^{n_p} \nu_p - 1 = 0, \tag{2.1.13d}$$

$$F_{n_c n_p + n_p + 1} = \sum_{c=1}^{n_c} z_c - 1 = 0, \tag{2.1.13e}$$

$$F_{k+n_c n_p + n_p + 1} = \prod_{p=1}^{n_p} \prod_{c=1}^{n_c} \alpha_{cp}^{v_{cq}} - K_q = 0. \qquad (q = 1, \ldots, n_q) \tag{2.1.13f}$$

After the secondary variables are obtained, the residual of the primary equation is updated to check if all the convergence criteria are satisfied. If not, the partial derivatives of the secondary variables, $\boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{S}}$, as a function of the primary variables, $\boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{P}}$, are required, and they are obtained by:

$$\frac{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{S}}}{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{P}}} = \left(\frac{\partial \mathbf{F}}{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{S}}} \right)^{-1} \frac{\partial \mathbf{F}}{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{P}}}. \tag{2.1.14}$$

$\dfrac{\partial \mathbf{F}}{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{S}}}$ is a square matrix, since the number of secondary variables is equal to the number of secondary equations. The most recent values of $\boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{P}}$ and $\boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{S}}$ are used to evaluate the $\dfrac{\partial \mathbf{F}}{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{S}}}$ and $\dfrac{\partial \mathbf{F}}{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{P}}}$ matrices. Then, $\boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{S}}$ and $\dfrac{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{S}}}{\partial \boldsymbol{\Upsilon}_{\mathbf{c}}^{\mathbf{P}}}$ are used to update the Jacobian of the primary equations. With the updated Jacobian and residual, the primary equations are solved for the primary variables. These steps are repeated until Newton convergence is achieved. Figure 2.1 summarizes the solution procedure of the overall-composition formulation for each Newton iteration.

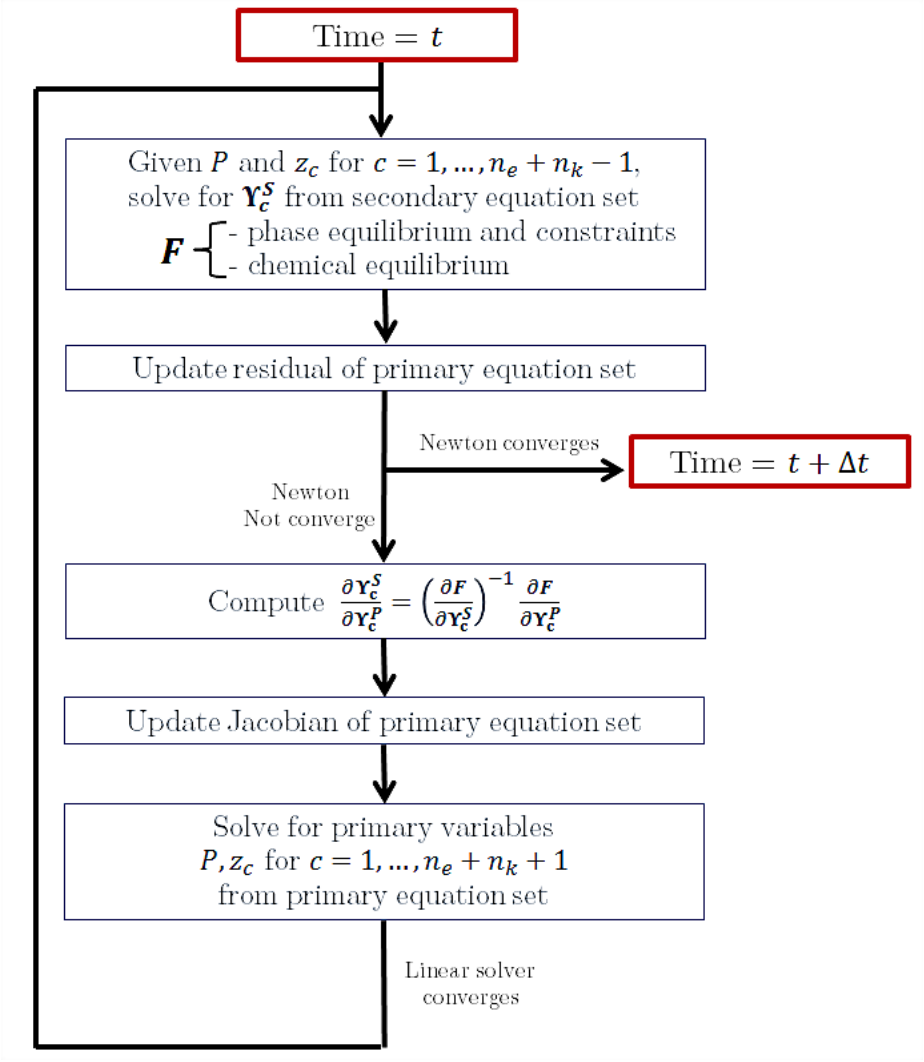


Figure 2.1: Flow chart for the solution procedure of the overall-composition formulation

2.2 Element formulation

In this section, the element formulation is obtained by making use of the relationship between the overall compositions and the elements to transform the element conservation equations written using the overall-composition variables to ones in terms of element variables.

2.2.1 Component-to-element transformation

The element fraction, $\mathbf{z_e}$, which is the ratio of moles of an element to the total moles of all elements, can be computed from the overall-composition fraction, $\mathbf{z_c}$, by using the component-to-element transformation, namely,

$$\mathbf{z_e} = \left(\frac{\rho_T}{\rho_T^E} \mathbf{E} \right) \mathbf{z_c}, \tag{2.2.1}$$

where ρ_T^E is the total element density. To guarantee uniqueness of the solution, the rank of the $\mathbf{E}$ matrix must be equal to the number of elements, n_e. So, the elements have to be chosen accordingly. Physically, ρ_T^E represents the total moles of all elements divided by the pore volume, which may be saturated by both solid and fluid phases, and it can be expressed as:

$$\rho_T^E = \sum_{p=1}^{n_p} \left(\rho_p S_p \sum_{c=1}^{n_c} \sum_{e=1}^{n_e} E_{ec} X_{cp} \right) = \frac{\displaystyle\sum_{c=1}^{n_c} \sum_{e=1}^{n_e} E_{ec} z_c}{\displaystyle\sum_{p=1}^{n_p} \frac{\nu_p}{\rho_p}}. \tag{2.2.2}$$

Here, E_{ec} is the number of element e in component c. By substituting the expression for ρ_T (Equation 2.1.4) and the expression for ρ_T^E (Equation 2.2.1) into the component-to-element transformation relation (Equation 2.2.1), one obtains

$$z_e = \frac{\sum_{c=1}^{n_c} E_{ec} z_c}{\sum_{c=1}^{n_c} \sum_{e=1}^{n_e} E_{ec} z_c} \qquad (e = 1, \ldots, n_e) . \tag{2.2.3}$$

From this, it can be easily observed that $\sum_{e=1}^{n_e} z_e = 1$.

2.2.2 Element-based governing equations

The component-to-element transformation is applied to the accumulation term of the element conservation equations written in terms of overall compositions, and that yields

$$\frac{\partial}{\partial t} \left(\hat{\phi} \rho_T^E \mathbf{z_e} \right) + \mathbf{EL} = 0. \tag{2.2.4}$$

This is the set of element conservation equations in terms of element variables. The accumulation term has very similar form to the one in the component conservation equations written in terms of overall composition variables (Equation 2.1.8), but with ρ_E^T replacing ρ_T and $\mathbf{z_e}$ replacing $\mathbf{z_c}$.

2.2.3 Molar variable set

In the element formulation, the following variable set is used:

$$\mathbf{\Upsilon_e} = (P, z_e, z_c, \nu_p, X_{cp}) \qquad (e = 1, \ldots, n_e, c = 1, \ldots, n_c \ \& \ p = 1, \ldots, n_p) . \tag{2.2.5}$$

Other variables are functions of $\mathbf{\Upsilon_e}$. It is important to note that there are n_e additional variables compared with the overall-composition formulation.

2.2.4 Solution strategies

Variable and equation types

The pressure P, element fractions z_e for $e = 1, \ldots, n_e - 1$, and overall composition fractions z_c for $c = 1, \ldots, n_k$, are chosen as the primary variables, which are denoted as $\mathbf{\Upsilon_e^P}$. Which z_c's to be used as the primary variables are yet to be investigated. The rest are the secondary variables, denoted as $\mathbf{\Upsilon_e^S}$. The primary equations are the same as the ones in the overall-composition formulation, namely, the n_e element conservation equations (Equation 2.1.9) and n_k kinetic reaction relations (Equation 2.1.10). When compared with the overall-composition formulation, $n_e - 1$ additional independent variables are introduced in this formulation. The degrees of freedom for the system are dictated by the Gibbs' phase rule regardless of the formulations used. Hence, the minimum number of primary variables and primary equations is fixed. Additional $n_e - 1$ secondary equations are needed. They come from the component-to-element transformation matrix (any $n_e - 1$ equations out of the total of n_e equations).

Table 2.3 summarizes the types of equations and variables in the element formulation.

Types	**Equations**	**Variables**
Primary	element conservation equations kinetic reaction relations	P z_e for $e = 1, \ldots, n_e - 1$ z_c for $c = 1, \ldots, n_k$
Secondary	equilibrium reaction relations phase-equilibrium and constraints component-to-element transformation	z_c for $c = n_k + 1, \ldots, n_c$ ν_p, X_{cp}

Table 2.3: Summary of types of equations and variables in the element formulation.

Solution procedure

The solution procedure for the element formulation is very similar to the one for the overall-composition formulation, since they are both members of the molar formulation family. There are two subtle differences. First, the phase behavior computation starts from a different set of primary variables. Also, in the element formulation, after the primary equations are solved to get the primary variables, the last z_e is obtained from the element constraint prior to solving the secondary equations. The element constraint is given by:

$$\sum_{e=1}^{n_e} z_e = 1. \tag{2.2.6}$$

When all the z_e's are known, this is analogous to knowing the distribution of each element in each of the grid blocks. Second, the secondary equation set, $\mathbf{F}$, for this element formulation also includes the component-to-element transformation in addition to the equation set listed in Equation 2.1.13. It is given by

$$F_{k+n_c n_p+n_p+n_q+1} = z_e - \frac{\rho_T}{\rho_T^E} E_e \mathbf{z_c} \qquad = 0 \qquad (e = 1, \ldots, n_e - 1)\,, \tag{2.2.7a}$$

where E_e denotes row e of $\mathbf{E}$. Note that z_c cannot be obtained readily from the component-to-element transformation (Equation 2.2.7), since n_e is, in general, less than n_c; hence, $\mathbf{E}$ is not square and is not invertible. The phase-equilibrium relations are still formulated in terms of components, not elements. When the secondary variables are computed, this is analogous to determining how the elements combine and form multiple components, and how the components partition across multiple phases. Figure 2.2 summarizes the solution procedure of the element formulation.

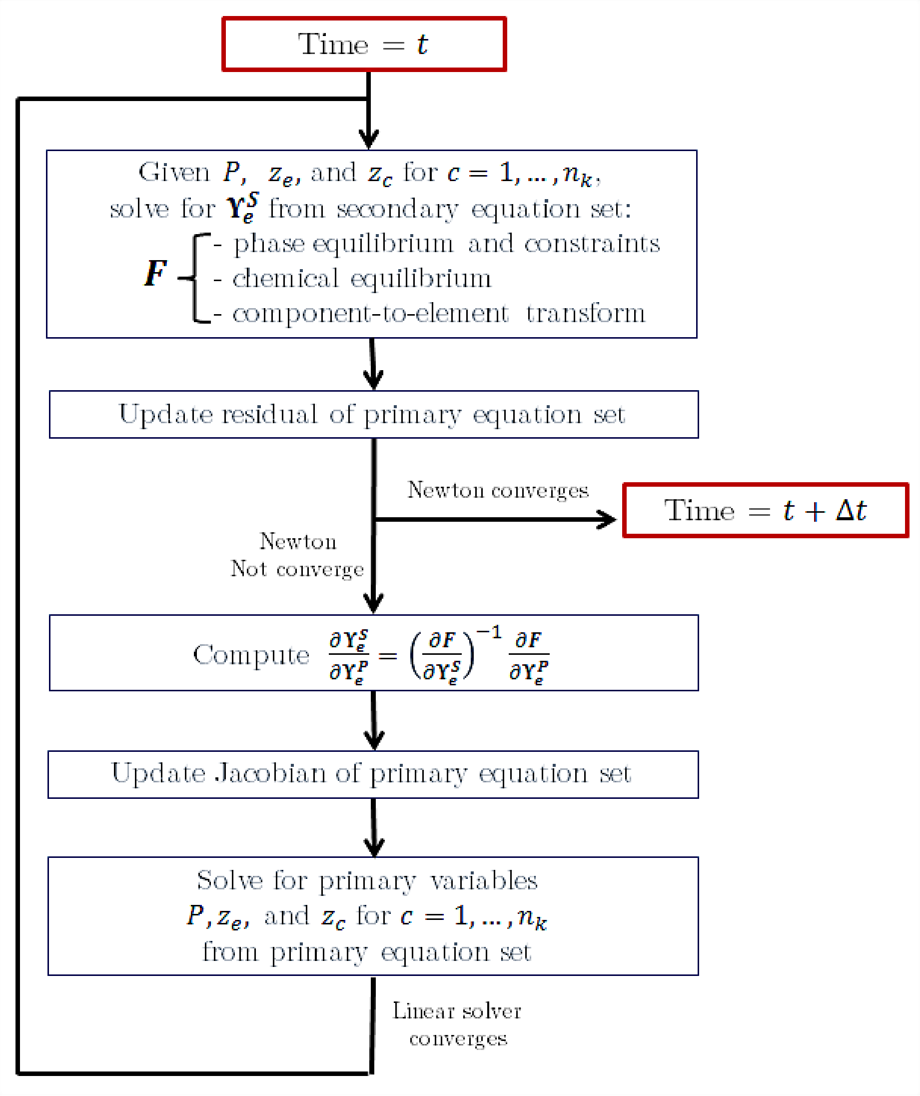


Figure 2.2: Flow chart for the solution procedure of the element formulation

2.3 Challenges in phase behavior computations

For the overall-composition formulation when chemical reactions are not included, P and all z_c's are known prior to solving the secondary equation set for the phase behavior. Various methods are available for performing phase-behavior computations. A two-stage procedure can be used [19]. In the first stage, the number of existing phases is determined for each grid block. This can be obtained by minimization of the Gibbs free-energy [25] or phase stability analysis based on the tangent plane distance (TPD) criterion [26]. In the second stage, flash calculations are performed to determine ν_p and X_{cp}. Other methods, such as the negative-flash approach [27] and Compositional Space Adaptive Tabulation (CSAT) [28], have also been proposed.

In cases with coupled chemical reactions, only some $n_e + n_k - 1$ of the z_c's are known for the overall-composition formulation, and the combination of z_e's and some n_k of z_c's are known in the element formulation prior to phase behavior computation. This poses an interesting challenge for using existing phase-behavior computation methods, since they are generally based on the requirement that P and all the z_c's are known. Though any flash calculation that can handle the presence of both phase and chemical equilibria may be applied, their usability depends on the ability to handle having an incomplete z_c set. In addition, phase equilibrium and chemical equilibrium are quite different. A phase-equilibrium relation describes how a single component partitions across two different phases. On the other hand, an equilibrium reaction relation describes the interaction among multiple components in, perhaps, multiple phases. Combining phase equilibrium and chemical equilibrium together results in additional challenges to phase behavior computation. Newton's method may be used, if an appropriate initial guess is available. Existing flash calculation algorithms have to be verified whether they are still valid in systems with combined phase and chemical equilibria. This subject has yet to be fully investigated.

It is worth noticing that the difference in the primary variables between the overall-composition and the element formulation results in different starting points for the phase-behavior computation and may result in different treatments for the two molar formulations.

2.4 Comparisons between natural-variables and molar formulations

The advantages and disadvantages of employing the two proposed molar formulations for coupled reaction systems compared with the natural-variables formulation are briefly discussed.

Jacobian matrix construction

To construct the Jacobian matrix, derivatives of the governing equations with respect to the variable set are required. In the natural-variables formulation, the derivatives can be calculated easily, since the governing equations are, naturally, in terms of the variable set. In the molar formulations, the derivatives are in more complicated expressions, and the difficulty in computing the Jacobian matrix is often cited as one of the main disadvantages of molar formulations. For coupled reaction problems, the matter is worse for molar formulations when complicated activity coefficient models and kinetic rate expressions are used. However, with the automatic differentiation functionality in AD-GPRS [24], the difficulties in calculating the derivatives for molar formulations are reduced significantly. This increases the attractiveness of using molar formulations for coupled reaction problems and opens up the possibility to evaluate them against the existing natural-variables formulation.

Variable substitution

In the natural-variables formulation, phase variables, including phase saturations, S_p, and phase compositions, X_{cp}, are used as primary variables. They have to be switched in and out of the primary variable set in response to phase appearance or disappearance in the grid block. This variable substitution procedure results in different primary variables for different grid blocks and adds complexity to the solution algorithms.

In the molar formulations proposed in this work, overall variables are used as primary variables, and they are the same for all the grid blocks. Thus, variable substitution is avoided. The phase behavior is dealt with separately when solving for the secondary variables. This may turn out to be beneficial, since the natural-variables formulation suffers from convergence issues as a result of aqueous phase disappearance [14].

Exact flash calculation

In the natural-variables formulation, the equilibrium phase behavior is obtained by converging the conservation equations, phase equilibrium, constraint relations, and chemical reaction relations simultaneously in the global Newton loop [24].

On the other hand, in molar formulations, exact flash calculation can be employed. Exact flash refers to the phase behavior computation in which the residuals of the local constraint relations are driven to zero separately from the residuals of the conservation equations. Exact flash computations in the proximity of the critical region have been investigated [21], but using this approach for combined phase and chemical equilibria has not been fully investigated.

Computational cost

The molar formulations require some additional phase behavior computations, which increase the computational cost. For example, assume that a maximum of two phases can be formed. In the natural-variables formulation, phase behavior computations are skipped for the two-phase grid blocks. In molar formulations, flash calculations cannot be skipped for two-phase grid blocks.

It is worth noting that the increase in the computational cost due to additional phase behavior computations may not be the main contributing factor to the total computational cost. Other factors, such as the number of timesteps taken, number of Newton iterations, and number of flash calculation iterations, are crucial, and they can be quite different when different formulations are used [21]. These factors are important when making performance comparisons among the different formulations for coupled reaction systems and should be validated.

Chapter 3

Model Construction, Results, and Discussion

3.1 Model problem

A simple model problem is used to understand the interactions between phase-equilibrium, reactions, and transport. The model is simple, but it is representative of more complex reactive transport problems. A one-dimensional (1D) porous medium is considered. The domain is fully saturated with salt ($NaCl$) water. CO_2 is injected from one end.

The model problem also has a real-world analogue: CO_2 injection induces and the dry-out effect. When water vaporizes into the gas phase, it leaves behind minerals in the vicinity of the injection well and reduces the well injectivity. Simulating the dry-out effect is challenging numerically as the time steps taken is controlled by how fast the aqueous components precipitate out of the aqueous phase. So, it may require many tiny time steps to be taken to complete the dry-out process [29].

Core-flood experiments and analytical solutions are available as benchmarks for the model problem. Ott et al. [30] injected dry supercritical CO_2 into a sandstone core that is pre-saturated with $NaCl$-based high-salinity brine and used Micro-Computed Tomography (μCT) scanning techniques to quantify the amount of $NaCl$ that precipitates due to CO_2 injection. The saturations of CO_2 and salt were recorded along the core. Zeidouni et al. [31], Pruess [32], and Noh et al. [33] approximated the dry-out process as occuring in a binary, gas-aqueous system and used fractional flow theory to derive analytical solutions. These analytical solutions can be used to check the accuracy of numerical simulations.

3.1.1 Model assumptions

The following important assumptions are made for the model problem studied in this chapter:

- Three components exist: CO_2 (ζ), H_2O (ω), and $NaCl$ (η). They can partition into three phases maximum: gas (g), aqueous (a), and solid (s) phases. Any phase combinations can be present in each grid block.

- The system is isothermal, and the phase equilibrium is specified by constant K-values.

- Only one chemical reaction is present: the equilibrium precipitation-dissolution reaction of $NaCl$ salt, and ideal conditions are assumed for all activity coefficients.

- Electrical neutrality is satisfied in the aqueous phase. Since in the aqueous phase, the number of moles of Na^+ ions is always equal to the number of moles of Cl^- ions, both are also equal to the number of moles of $NaCl$ (aq). Na^+ and Cl^- ions are accounted for $NaCl$ as a component in the aqueous phase.

- Capillary pressure, hydrodynamic dispersion, and gravitational force are neglected.

- Fluid phase relative permeability is a quadratic function of phase saturation.

- No volume-change on mixing.

There are a few possible ways to designate the “elements” in this problem. Here, three independent elements are chosen: C represents carbon atoms, O represents oxygen atoms, and N represents $NaCl$. The element stoichiometric matrix $\mathbf{E}$ is, then, given by:

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.1.1}$$

The first, second, and third rows correspond to C, O, and N respectively, while the first, second, and third columns correspond to ζ, ω, and η respectively. The rank of $\mathbf{E}$ is three, which is equal to the number of elements.

3.1.2 Governing equations

Element conservation equations

The primary equations for the system are the element conservation equations written in terms of element variables. They are written in the concise format as:

$$\frac{\partial}{\partial t}\left(\hat{\phi}\rho_T^E \mathbf{z_e}\right) + \mathbf{EL} = 0, \tag{3.1.2}$$

where $\mathbf{z_e} = (z_C, z_O, z_N)^T$. $\mathbf{L}$ is given by:

$$\mathbf{L} = \sum_{\text{existing fluid } p} \begin{bmatrix} \frac{\partial}{\partial x}\left(\rho_p X_{\zeta p} u_p\right) \\ \frac{\partial}{\partial x}\left(\rho_p X_{\omega p} u_p\right) \\ \frac{\partial}{\partial x}\left(\rho_p X_{\eta p} u_p\right) \end{bmatrix}, \tag{3.1.3}$$

where $\rho_p = \left(\sum_{c=1}^{n_c} \frac{X_{cp}}{\rho_c}\right)^{-1}$, since linear volume mixing is assumed. It should be emphasized that the summation in $\mathbf{L}$ is over the existing fluid phases only. The 1D Darcy velocity u_p is given by:

$$u_p = -\frac{k k_{rp}}{\mu_p}\frac{\partial P}{\partial x}. \tag{3.1.4}$$

Chemical equilibrium relation

The interaction between $NaCl$ (aq) and $NaCl$ (s) is governed by an equilibrium precipitation-dissolution reaction instead of a phase-equilibrium K-value. The equilibrium reaction can be written as:

$$NaCl(s) \leftrightarrow Na^+(aq) + Cl^-(aq). \tag{3.1.5}$$

The law of mass action governing this equilibrium reaction is given by:

$$K_q = \prod_{p=1}^{n_p}\prod_{c=1}^{n_c} \alpha_{cp}^{v_{cq}} = \alpha_{Na^+,a}\alpha_{Cl^-,a}. \tag{3.1.6}$$

The activity of solid $NaCl$ is set to one by definition for a pure mineral. For molality-type activity, the chemical activity of an aqueous component c (except water) in the aqueous phase a is given by [16]:

$$\alpha_{ca} = 55.508\left(\frac{\gamma_{ca}X_{ca}}{X_{\omega a}}\right), \tag{3.1.7}$$

where γ_{ca} represents the activity coefficient of component c in the aqueous phase a. In this expression, 55.508 is the number of moles of H_2O per kilogram. Equation 3.1.6 can now be written as:

$$K_q = 55.508^2\gamma_{Na^+,a}\gamma_{Cl^-,a}\left(\frac{X_{Na^+,a}X_{Cl^-,a}}{X^*_{\omega a}}\right)^2, \tag{3.1.8}$$

where $X^*_{\omega a}$ is the composition of H_2O in the aqueous phase that consists of H_2O, Na^+, and Cl^-, for which moles of Na^+ and Cl^- are separately accounted. $X_{\omega a}$ refers to the composition of H_2O in the aqueous phase that consists of H_2O and $NaCl$ (aq). Using the definition of phase compositions and the electrical neutrality condition, it can be shown that

$$X^*_{\omega a} = \frac{X_{\omega a}}{1+X_{\eta a}}, \tag{3.1.9a}$$

$$X_{Na^+,a} = \frac{X_{\eta a}}{1+X_{\eta a}}, \tag{3.1.9b}$$

$$X_{Cl^-,a} = \frac{X_{\eta a}}{1+X_{\eta a}}. \tag{3.1.9c}$$

Equation 3.1.9 is substituted into the equilibrium reaction relation (Equation 3.1.6). The final form of the equilibrium reaction relation for the model problem is obtained:

$$K_q = 55.508^2\gamma_{Na^+,a}\gamma_{Cl^-,a}\left(\frac{X_{\eta a}}{X_{\omega a}}\right)^2, \tag{3.1.10}$$

$$\Theta_q = \sqrt{\frac{55.508^2\gamma_{Na^+,a}\gamma_{Cl^-,a}}{K_q}} = \frac{X_{\omega a}}{X_{\eta a}}. \tag{3.1.11}$$

Θ_q looks similar to a phase-equilibrium K-value, yet they are quite different. Θ_q connects two different components in the same aqueous phase, while a phase-equilibrium K-value connects a component across two different phases.

Component-to-element constraints

Starting with the component-to-element transformation expression (Equation 2.2.1), and after some rearrangement, the component-to-element constraints become:

$$\left(\mathbf{E} - \begin{bmatrix} z_C \\ z_O \\ z_N \end{bmatrix} \begin{bmatrix} \sum_{e=1}^{n_e} E_{e\zeta} & \sum_{e=1}^{n_e} E_{e\omega} & \sum_{e=1}^{n_e} E_{e\eta} \end{bmatrix} \right) \begin{bmatrix} z_\zeta \\ z_\omega \\ z_\eta \end{bmatrix} = 0, \tag{3.1.12}$$

$$\begin{bmatrix} 1-3z_C & -z_C & -z_C \\ 2-3z_O & 1-z_O & -z_O \\ -3z_N & -z_N & 1-z_N \end{bmatrix} \begin{bmatrix} z_\zeta \\ z_\omega \\ z_\eta \end{bmatrix} = 0. \tag{3.1.13}$$

Any two out of the three equations can be selected as the independent component-to-element constraints.

Phase-equilibrium and constraint relations

In general, $n_c(n_p - 1)$ phase-equilibrium relations can be defined for a system of n_c components and n_p phases, if any component can exist in any phase. Before any simplification is made, the model problem has five components: CO_2, H_2O, Na^+ ions, Cl^- ions, and $NaCl$ mineral. If any component can exist in any phase, then ten phase-equilibrium relations must be defined. Two simplifications are made to the phase behavior. First, the $NaCl$ mineral is assumed to reside only in the solid phase. Second, the Na^+ and Cl^- ions are assumed not to reside in the solid phase. With these two assumptions, the number of phase-equilibrium relations is reduced to six. Then, when the electrical neutrality condition is applied, the Na^+ and Cl^- ions are treated as a single component, namely, $NaCl$. From the two gas-aqueous phase-equilibrium relations for the Na^+ ion and the Cl^- ion, only one is needed for $NaCl$. The result is that only five phase-equilibrium relations are required. A phase-equilibrium relation between $NaCl$ (s) and $NaCl$ (aq) ions is not needed because they come from different components: the $NaCl$ mineral for $NaCl$ (s), and the $Na^+ + Cl^-$ ions for $NaCl$ (aq). Instead, the relationship between the two is governed by an equilibrium chemical reaction. The five phase-equilibrium relations for the model problem are:

$$K_\zeta^s = \frac{X_{\zeta s}}{X_{\zeta a}}, \qquad K_\zeta^g = \frac{X_{\zeta g}}{X_{\zeta a}}, \tag{3.1.14a}$$

$$K_\omega^s = \frac{X_{\omega s}}{X_{\omega a}}, \qquad K_\zeta^g = \frac{X_{\omega g}}{X_{\omega a}}, \tag{3.1.14b}$$

$$K_\eta^g = \frac{X_{\eta g}}{X_{\eta a}}, \tag{3.1.14c}$$

The phase-constraint relations are: three overall mole fraction constraints, two phase molar constraints, one molar phase fraction constraint, and one overall composition constraint.

3.1.3 Solution strategies

The finite-volume method with fully-implicit time discretization is used. The solution strategies of the model problem follows the element formulation strategies described in the previous chapter. Since there are no kinetic reactions, the primary equations are only the element conservation equations. The rest of the equations, including the chemical-equilibrium relation, component-to-element constraint, phase-equilibrium, and constraint relations, make up the secondary equations. The primary variables are P and any two of the three z_e's. The simulation procedure for each

Newton iteration is exactly as shown in Figure 2.2.

3.1.4 Phase behavior computation

The starting point of the phase behavior computation is P and $\mathbf{z_e}$. A simple two-step procedure is implemented to compute the phase behavior of the model problem.

Phase state identification

Phase behavior computations are different for different sets of coexisting phases. The negative-flash [27] approach is used to determine the phase state. Though the negative-flash approach has been shown to encounter convergence issues near critical points, such points do not exist in the model problem. In the negative-flash approach, the phase state is based on the signs of the phase molar fractions, ν_p. First, Newton's method is applied on the full set of the secondary equations in order to obtain the signs of ν_p. Newton's method on the full set of secondary equations can be computationally expensive. For systems that involve only phase equlibrium, two Rachford-Rice equations for three-phase system are often recommended instead, provided $\mathbf{z_c}$ and K-values, as well as, appropriate lower and upper bounds for the bisection, or Newton's method, are provided [27, 34]. However, there are two critical issues with formulating the Rachford-Rice-based equations when applied to the combined phase and chemical equilibria. First, some z_c's are generally not known. Second, though there is a general form of the Rachford-Rice-based equations for phase-equilibrium systems, there is no general form when equilibrium reactions are present because the form is system-specific. When some components are involved in both phase equilibrium and chemical equilibrium, it may be impossible to derive Rachford-Rice-based equations, not to mention how to specify appropriate lower and upper bounds. So, the Rachford-Rice approach is not recommended for coupled reaction problems.

Newton's method generally relies on a good initial guess, but for the application of Newton's method on the model problem the issue with the initial guess does not arise.

After the signs of ν_p are known, the phase state is defined from the following binary formula as in AD-GPRS [24].

$$N_{\#} = \sum_{p=1}^{n_p} 2^{p-1} \delta_{(\nu_p > 0)}, \tag{3.1.15}$$

where $\delta_{(\nu_p>0)} = 1$ if $\nu_p > 0$, and 0 otherwise. There are seven possible phase states for the three-phase system as summarized in Table 3.1.

State ($N_{\#}$)	**Number of phases**	**Gas phase**	**Aqueous phase**	**Solid phase**
1	1	✓	-	-
2	1	-	✓	-
3	2	✓	✓	-
4	1	-	-	✓
5	2	✓	-	✓
6	2	-	✓	✓
7	3	✓	✓	✓

Table 3.1: Phase-state combinations for a three-phase system

Flash calculation

After the phase state is known, the phase variables ν_p, X_{cp}, and z_c can be obtained. This step handles different phase-state combinations differently as explained below:

1. **Single phase**: since all the components are in the same phase, $X_{cp} = z_c$ and $\nu_p = 1$ for the phase.

2. **Two phases**: Newton's method is applied again on a subset of secondary equations. Which of the secondary equations are included depends on the co-existing phases. If it turns out that one of the two ν_p's is less than zero, the system is actually single-phase. Special details for each two-phase state combinations are discussed in the following section.

3. **Three phases**: For this simple constant K-value problem, X_{cp} obtained from the previous step corresponds to the three corners of the three-phase region regardless of the phase state, and ν_p is already determined.

Following the phase behavior computation, the residual and the Jacobian matrix of the primary set can be updated.

3.2 Results and discussions

3.2.1 Phase behavior

Results observed when performing the phase behavior computation are discussed, including the effects of trace compositions and the starting points for the phase behavior computation.

Trace compositions

The element formulation allows any component to exist in any phase. A decision has to be made whether, or not, to include some components in some of the phases. Trace compositions for the model problem refers to CO_2 and H_2O components in the solid phase and the $NaCl$ component in the gas phase. It is debatable whether the trace compositions physically exist or not. It is also not known if including the trace compositions would be beneficial numerically for coupled reaction systems or would introduce some unphysical results.

Case 1: Excluding trace compositions

In this case, when the full three-phase system (state 7) is considered, there are three equilibrium relations to close the system: two phase-equilibrium relations ($\Leftrightarrow$) and one equilibrium reaction relation ($\leftrightarrow$), as shown in Table 3.2. The equilibrium reaction relation governs the amount of $NaCl$ in the solid and the aqueous phases.

Components	Gas phase		Aqueous phase	Solid phase
CO_2	✓	$\Leftrightarrow$	✓	-
H_2O	✓	$\Leftrightarrow$	✓	-
			$\updownarrow$	
$NaCl$	-		✓	✓

Table 3.2: Three-phase compositions table when trace compositions are excluded.

When only the gas and the aqueous phases exist (state 3), the compositions table is as shown in Table 3.3. CO_2 and H_2O reside in both the gas and aqueous phases, so two phase-equilibrium relations are required. Note that $NaCl$ lives only in the aqueous phase. The precipitation-dissolution reaction relation is ignored, as it has no physical meaning when the aqueous phase and the solid phases do not coexist.

Components	Gas phase		Aqueous phase
CO_2	✓	$\Leftrightarrow$	✓
H_2O	✓	$\Leftrightarrow$	✓
$NaCl$	-		✓

Table 3.3: State 3 compositions table when trace compositions are excluded.

When only the gas and the solid phases exist (state 5), a component resides in only one phase, as shown in Table 3.4. None of the equilibrium relations is needed.

Components	**Gas phase**	**Solid phase**
CO_2	✓	-
H_2O	✓	-
$NaCl$	-	✓

Table 3.4: State 5 compositions table when trace compositions are excluded.

When only the aqueous and the solid phases exist (state 6), CO_2 and H_2O are present in the aqueous phase, so the phase-equilibrium relations are not needed. $NaCl$ resides in both the aqueous phase and the solid phase, and the equilibrium reaction relation is used to describe the partitioning of $NaCl$ as shown in Table 3.5.

Components	**Aqueous phase**	**Solid phase**
CO_2	✓	-
H_2O	✓	-
	$\updownarrow$	
$NaCl$	✓	✓

Table 3.5: State 6 compositions table when trace compositions are excluded.

The results of the phase behavior computation can be shown on a ternary diagram. The vertices of the ternary diagram represent the pure three components, CO_2, H_2O, and $NaCl$. There are seven regions, corresponding to seven phase states. The single-phase regions are around the three vertices. The two-phase regions are along the three edges. The three-phase region is in the middle. The corners of the three-phase region are always at the same locations for this constant K-value system.

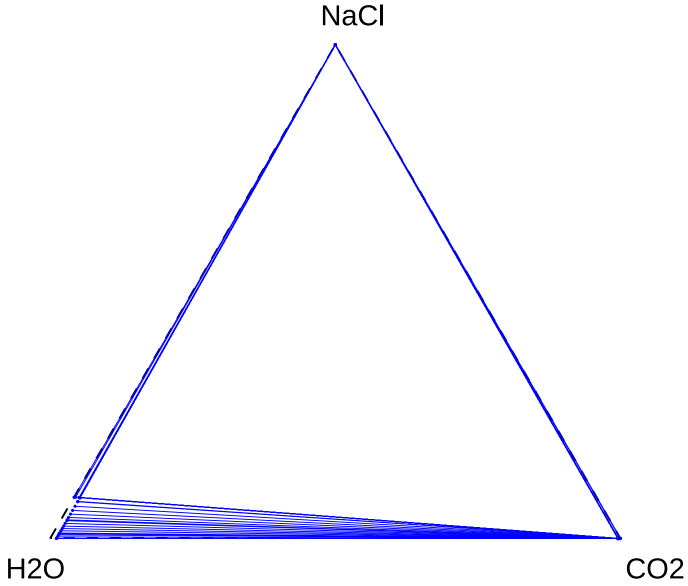


Figure 3.1: Ternary diagram when trace compositions are excluded

Case 2: Including trace compositions

In this case, three trace compositions are introduced: $X_{\zeta s}$, $X_{\omega s}$, and $X_{\eta g}$. When the full three-phase system (state 7) is considered, there are six equilibrium relations to close the system: five phase-equilibrium relations ($\Leftrightarrow$) and one equilibrium reaction relation ($\leftrightarrow$), as shown in Table 3.6. Three new phase-equilibrium relations are introduced to describe the presence of the three trace compositions. The amounts of the trace compositions are controlled by three K-values (K_{ζ}^{s}, K_{ω}^{s}, and K_{η}^{g}).

Components	**Gas phase**		**Aqueous phase**		**Solid phase**
CO_2	✓	$\Leftrightarrow$	✓	$\Leftrightarrow$	✓
H_2O	✓	$\Leftrightarrow$	✓	$\Leftrightarrow$	✓
			$\updownarrow$		
$NaCl$	✓	$\Leftrightarrow$	✓		✓

Table 3.6: Three-phase compositions table when trace compositions are included.

When only the gas and the aqueous phases exist (state 3), the compositions table is shown in Table 3.7. Note that CO_2, H_2O, and $NaCl$ reside in both the gas and aqueous phases, so that three phase-equilibrium relations are required. Similar to the previous case, the precipitation-dissolution reaction relation is ignored, since the aqueous phase and the solid phase are not both present.

Components	**Gas phase**		**Aqueous phase**
CO_2	✓	$\Leftrightarrow$	✓
H_2O	✓	$\Leftrightarrow$	✓
$NaCl$	✓	$\Leftrightarrow$	✓

Table 3.7: State 3 compositions table when trace compositions are included.

When only the gas and the solid phases exist (state 5), none of the equilibrium relations that were previously defined can be used directly (Table 3.8). In order to be consistent with the original equilibrium relations, the following three new relations are derived for the constant K-value system:

$$K_\zeta^{gs} = \frac{X_{\zeta g}}{X_{\zeta s}} = \frac{K_\zeta^g}{K_\zeta^s}, \tag{3.2.1a}$$

$$K_\omega^{gs} = \frac{X_{\omega g}}{X_{\omega s}} = \frac{K_\omega^g}{K_\omega^s}, \tag{3.2.1b}$$

$$K_\eta^{gs} = \frac{X_{\eta g}}{X_{\omega s}} = \frac{K_\eta^g}{K_\omega^s \Theta_q}. \tag{3.2.1c}$$

Components	**Gas phase**	**Solid phase**
CO_2	✓	✓
H_2O	✓	✓
$NaCl$	✓	✓

Table 3.8: State 5 compositions table when trace compositions are included.

When only the aqueous and solid phase exist (status 6), two phase-equilibrium relations for CO_2 and H_2O and one equilibrium reaction relation are used to completely determine the phase behavior, as shown in Table 3.9.

Components	**Aqueous phase**		**Solid phase**
CO_2	✓	⇔	✓
H_2O	✓	⇔	✓
	↕		
$NaCl$	✓		✓

Table 3.9: State 6 compositions table when trace compositions are included.

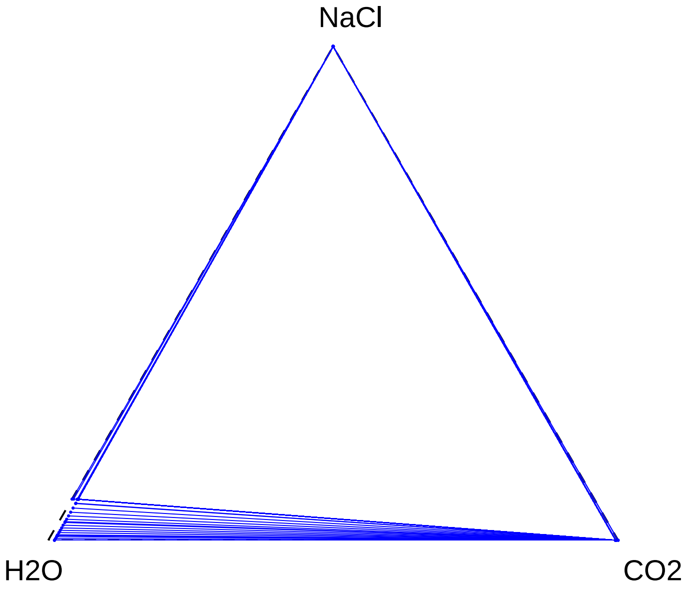


Figure 3.2: Ternary diagram when trace compositions on the order of $O(10^{-5})$ are present.

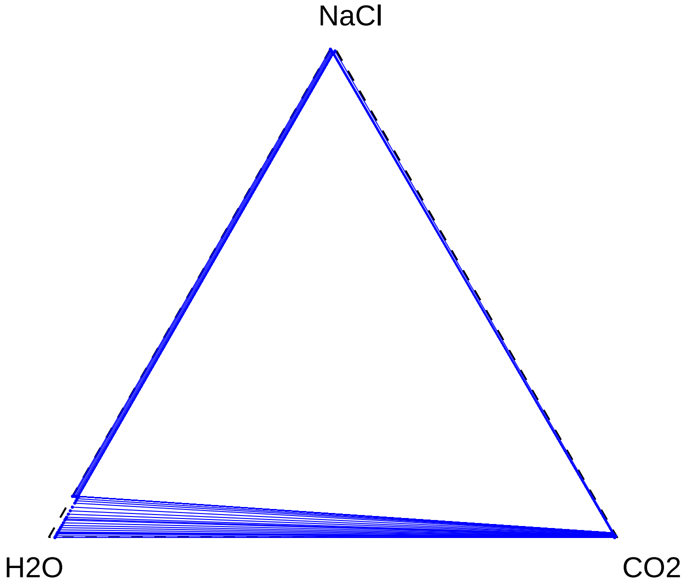


Figure 3.3: Ternary diagram when trace compositions on the order of $O(10^{-2})$ are present.

The results of the phase behavior computations suggest that if the trace compositions are sufficiently small, including or excluding them gives similar results, as indicated by Figures 3.1 and 3.2. If the trace compositions are not small enough, the phase behavior can be different as observed in Figure 3.3. The corners of the three phase region shift inwards, away from the edges of the ternary diagram.

Starting points for phase behavior computation

The starting points for the phase behavior computations can be either the element fractions ($\mathbf{z_e}$), or the overall composition fractions ($\mathbf{z_c}$).

Case 1: Starting from $\mathbf{z_e}$ In this case, $\mathbf{z_e}$ is assumed to be known prior to the phase behavior computation. The following linear constraints have to be met:

$$z_e \leq 1 \qquad (e = C, O, N), \tag{3.2.2a}$$

$$z_C - 2z_O \leq 0, \tag{3.2.2b}$$

$$\sum_{n_e=1}^{3} z_e = 1. \tag{3.2.2c}$$

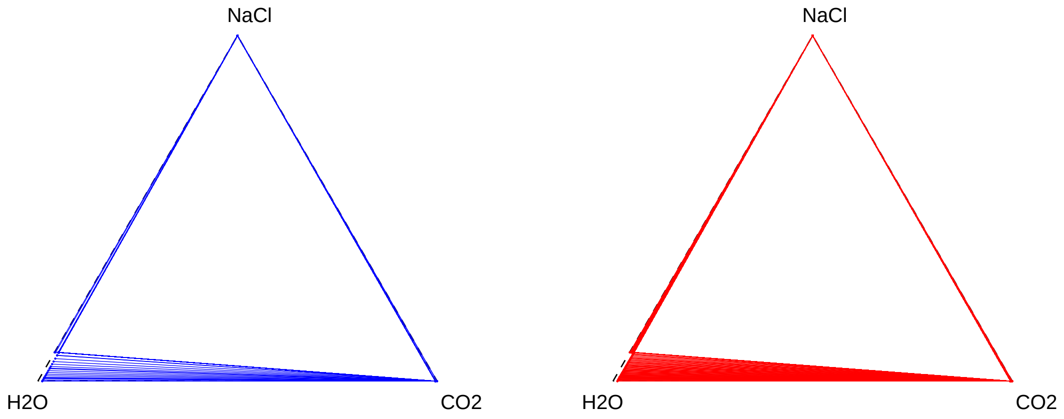
The moles of the O element have to be at least twice as many as the moles of the C element; otherwise, some C elements are left over as C atoms instead of combining with O atoms and forming CO_2.

Case 2: Starting from $\mathbf{z_c}$ In this case, $\mathbf{z_c}$ is assumed to be known. The component-to-element constraints (Equation 3.1.13) and the overall composition constraint are neglected. The initial overall composition can be anywhere in the compositional space, which means that the following linear constraints are met:

$$z_c \leq 1 \qquad (c = \zeta, \omega, \eta), \tag{3.2.3a}$$

$$\sum_{n_c=1}^{3} z_c = 1. \tag{3.2.3b}$$

The two cases are compared in Figure 3.4. The ternary diagrams of the two cases look similar. Hence, starting from element fractions gives phase behavior results that are identical to the case of starting with the overall compositions. In order to plot a ternary diagram with phase boundaries and multiple tie-lines, the starting points are varied in order to cover the whole space that satisfies the linear constraints described above. No convergence issues are observed. This suggests that the two-step procedure used is robust for this model problem; that is, from any $\mathbf{z_c}$ and $\mathbf{z_e}$, the phase behavior can be resolved.



(a) starting from $\mathbf{z_c}$

(b) starting from $\mathbf{z_e}$

Figure 3.4: Comparison of ternary diagrams with different starting points for phase computation

Chapter 4

Conclusions and Future Work

4.1 Conclusions

In this work, two element-based, molar formulations for coupled flow, transport, and chemical reactions are proposed, namely, the overall-composition formulation and the element formulation. Both formulations have a general treatment of the solid phase and are generalized such that any component can exist in any phase.

In the overall-composition formulation, the primary equations are the element conservation equations and the kinetic reaction relations. The primary variables are the pressure and a subset of the overall-composition fractions. In the element formulation, the primary equations are also the element conservation equations and the kinetic reaction relations. The primary variables are the pressure, all of the element fractions, and a subset of the overall-composition fractions.

The two formulations are different from the standard natural-variables formulation in several important ways. In cases of phase appearance and disappearance, the proposed formulations do not require variable substitution, because none of the phase variables are primary variables. In order to obtain the phase behavior, exact flash calculations are used to solve the secondary equations, which consist of both phase equilibrium and chemical equilibrium relations.

A model problem is constructed such that it is simple to check the results against physical experiments and analytical solutions, but it is representative of more complex problems with coupled reactions. The model describes one-dimensional CO_2 injection into salt ($NaCl$) water and only one equilibrium precipitation-dissolution reaction of $NaCl$ salt is involved. The element formulation is employed, and a two-step phase behavior computation procedure is developed specifically for the model problem.

The results of the phase behavior computation show that excluding or including the trace compositions give very similar results. The starting points of the phase computation can be either the overall-composition fractions, $\mathbf{z_c}$, or the element fractions, $\mathbf{z_e}$. The two result in identical phase behaviors. It is also shown that from any starting $\mathbf{z_c}$ or $\mathbf{z_e}$, the phase behavior can be resolved.

4.2 Recommendations for future work

There are various ways to build on this research work. Some are listed below:

1. The primary variables of both the overall-composition formulation and the element formulation consist of a subset of overall compositions, $\mathbf{z_c}$. It should be investigated which z_c's are more appropriate to be used as the primary variables.

2. Chemical equilibrium and phase equilibrium are coupled in the secondary equations of the two molar formulations, and success of the molar formulations relies on accurate exact flash calculation designed for coupled phase and chemical equilibria. In some cases, it may be possible to decouple the two equilibria from each other. However, in cases that chemical reactions and the thermodynamic phase equilibrium are tightly coupled, accurate and efficient methods for phase behavior computation are needed.

3. The simulation results in Chapter 3 are based on a long list of simplifying assumptions. Many of the assumptions can be relaxed, for example,
    - Instead of using constant K-values, more realistic phase equilibrium models should be introduced. The first step is to allow the K-values to vary with pressure. Complicated EOS models can, then, be incorporated.
    - The precipitation-dissolution reaction may be modified, such that it is a kinetic reaction, instead of an equilibrium reaction. Other relevant equilibrium chemical reactions, e.g., the dissociation of CO_2 in the aqueous phase, and the protolysis of water, can also be included.
    - Additional physical processes, such as capillary pressures and the gravitational force, may be incorporated into the model problem. So, the effects of coupling chemical reaction with other physical processes can be studied. For example, capillary pressure has been noted to noticeably increase the solid-phase saturation near the injection well by capillary-driven backflow of the aqueous phase toward the injection well [35]. Additionally, if the model is extended to multiple dimensions and the gravitational force is included, the effect of coupling between chemical reactions and convective mixing of dissolved CO_2 can be studied.
4. After the robustness of the two molar formulations is verified, they should be evaluated against the standard natural-variables formulation.
5. There are interesting systems where the effect of temperature on both the phase equilibrium, and the reaction rates may be important. Handling such systems would require extending the element-based formulations to thermal problems.

Bibliography

[1] Fan Y., Durlofsky L.J., and Tchelepi H.A. A fully-coupled reactive-transport formulation based on element conservation, with application to CO2 storage simulations. *Advances in Water Resources*, 42:47–61, 2012.

[2] Nghiem L.X., Fong D.K., Aziz K. Compositional modeling with an equation of state. *SPE Journal*, 21:687–698, 1981.

[3] Cao H. *Development of techniques for general purpose reservoir simulators.* PhD thesis, Department of Energy Resources Engineering. Stanford University, California, 2002.

[4] Coats K.H. SPE 8284: An Equation of State Compositional Model. *SPE Journal*, 1980.

[5] Young L.C., Stephenson R.E. SPE 10516: A generalized compositional approach for reservoir simulation. *SPE Journal*, 1983.

[6] Lu J., Goudarzi A., Chen P., Kim D.H., Britton C., Delshad M., Mohanty K.K., Weerasooriya U.P., Pope G.A. SPE 159979: Modeling aqueous phase behavior and chemical reactions in compositional simulation. *SPE Annual Technical Conference and Exhibition. San Antonio, Texas*, 2012.

[7] Nghiem L.X., Shrivastava V., Kohse B. SPE 141417: Modeling aqueous phase behavior and chemical reactions in compositional simulation. *SPE Reservoir Simulation Sysmposium. Woodlands, Texas*, 2011.

[8] Computer Modelling Group. GEM-GHG. *Technical Documentation*, 2010.

[9] Lichtner P.C. Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems. *Geochimica et Cosmochimica Acta*, 49(3):779–800, 1985.

[10] Yeh G.T., Tripathi V.S. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resources Research*, 25(1):93–108, 1989.

[11] Yeh G.T., Tripathi V.S. A model for simulating transport of reactive multispecies components: model development and demonstration. *Water Resources Research*, 27(12):3075–3094, 1991.

[12] Steefel C.I., Lasaga A.C. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. *American Journal of Science*, 294:529–592, 1994.

[13] Steefel C.I., DePaolo D.J., Lichtner P.C. Reactive transport modeling: An essential tool in a new research approach for the earth sciences. *Earth and Planetary Science Letters*, 240:539–558, 2005.

[14] Farshidi S.F., Fan Y., Durlofsky L.J., Tchelepi H.A. SPE 163677: Chemical reaction modeling in a compositional reservoir-simulation framework. *SPE Reservoir Simulation Symposium. Woodlands, Texas*, 2013.

[15] Lake L.W. *Enhanced Oil Recovery.* Prentice Hall, New Jersey, 1989.

[16] Fan Y. *Chemical reaction modeling in a subsurface flow simulator with application to in-situ upgrading and CO2 mineralization.* PhD thesis, Department of Energy Resources Engineering. Stanford University, California, 2010.

[17] Lichtner P.C. Continuum formulation of multicomponent-multiphase reactive transport. In Lichtner, P.C., Steefel, C.I., Oelkers, E.H., editor, *Reactive transport in porous media*. The Mineralogical Society of America, Washington, D.C., 1996.

[18] Palandri J.L., Kharaka Y.K. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. *US. Geological Survey Open File Report*, 1068, 2004.

[19] Voskov D.V., Younis R.M., Tchelepi H.A. SPE 118996: General nonlinear solution strategies for multiphase multicomponent EoS based simulation. *SPE Reservoir Simulation Symposium. Woodlands, Texas*, 2009.

[20] Aziz K., Wong T.W. Considerations in the development of multipurpose reservoir simulation models. *proceedings of the First and Second International Forum on Reservoir Simulation, Alpbach, Austria*, 1998-99.

[21] Voskov D.V., Tchelepi H.A. Comparison of nonlinear formulations for two-phase multi-component EoS based simulation. *Journal of Petroleum Science and Engineering*, 2012.

[22] Chien M.C.H., Lee S.T., Chen W.H. SPE 13385: A new fully implicit compositional simulator. *Eight SPE Symposium on Reservoir Simulation, Dallas, Texas*, 1985.

[23] Acs G., Doleschall S., Farkas E. General purpose compositional model. *SPE Journal*, pages 543–553, 1985.

[24] Voskov D.V., Zhou Y., Aziz K. AD-GPRS Stanford University's Automatic Differentiation based General Purpose Research Simulator. *Technical Documentation*, 2012.

[25] Gautam R., Seider W.D. Computation of phase and chemical equilibrium. *AlChE Journal*, 1979.

[26] Michelsen M.L. The isothermal flash problem: Part I. Stability. *Fluid Phase Equilibria*, 9:1–19, 1982.

[27] Iranshahr A., Voskov D.V., Tchelepi H.A. Generalized negative-flash method for multiphase multicomponent systems. *Fluid Phase Equilibria*, 2:272–284, 2010.

[28] Voskov D.V., Tchelepi H.A. Compositional space parametrization: multicontact miscible displacements and extension to multiple phases. *SPE Journal*, 14(3), 2009.

[29] Zhang G., Spycher N., Xu T., Sonnenthal E., Steefel C. Reactive geochemical transport modeling of concentrated aqueous solutions: supplement to TOUGHREACT user's guide for the Pitzer's ion-interation model. *Earth Sciences Division, Lawrence Berkeley National Laboratory*, 2006.

[30] Ott H., de Kloe K., Marcelis F., Makurat A. Injection of supercritical CO2 in brine saturated sandstone: Pattern formation during salt precipitation. *Energy Procedia*, 4:4425–4432, 2011.

[31] Zeidouni M., Pooladi-Darvish M., Keith D. Analytical solution to evaluate salt precipitation during CO2 injection in saline aquifers. *International Journal of Greenhouse Gas Control*, 3:600–611, 2009.

[32] Pruess K. Formation dry-out from CO2 injection into saline aquifers: 2. Analytical model for salt precipitation. *Water Resources Research*, 45, 2009.

[33] Noh M., Lake L.W., Bryant S.L., Araque-Martinez A. Implications of coupling fractional flow and geochemistry for CO2 injection in aquifers. *SPE Reservoir Evaluation and Engineering*, 10:406–414, 2007.

[34] Haugen K.B., Sun L., Firoozabadi A. SPE 106045: Three-phase equilibrium calculations for compositional simulation. *SPE Reservoir Simulation Symposium. Houston, Texas*, 2007.

[35] Pruess K., Muller N. Formation dry-out from CO2 injection into saline aquifers: 1. Effects of solids preciptation and their mitigation. *Water Resources Research*, 45, 2009.