“Non-linearities and upscaling in porous media“

Master’s Thesis

Investigation of a decoupling scheme for the modeling of reactive transport

Naibin Song

Supervisors:
Johannes Hommel
Rainer Helmig
Holger Class

Preprint 2014/1
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Nomenclature

D Damköhler number

$V_{\text{pore}}$ Volume of pore space in REV.

$V_{\text{total}}$ Total volume of REV.

A Parameter for Debye-Hückel equation

B Parameter for Debye-Hückel equation

C Mass concentration

I Ionic strength

$\text{CO}_3^{2-}$ Carbonate

$C_{\text{tot}}$ Sum of carbon dioxide dissolved in the water, bicarbonate and carbonate ions.

$\text{Ca}^{2+}$ Calcium ion

$\text{CaCO}_3$ Calcite

$\text{Cl}^{-}$ Chloride ion

$\text{CO}_2$ Carbon dioxide

$\text{H}^{+}$ Hydrogen ion

$\text{H}_2\text{CO}_3$ Carbonic acid

$\text{HCO}_3^{-}$ Bicarbonate

$\text{Na}^{+}$ Sodium ion
OH\(^-\)  Hydroxide ion
X\(^{al}\)  Salinity of the brine
Ω  Calcite saturation state
\(D_{pm}\)  Diffusion coefficient within the porous medium
\(E_c\)  Coupling error
\(K\)  Permeability tensor
\(K_0\)  Initial permeability
\(K_1\)  Dissociation constant for carbonic acid
\(K_2\)  Dissociation constant for bicarbonate
\(K_{CaCO_3}\)  Calcite solubility product
\(K_w\)  Dissociation constant for water
\(K_{eq}\)  Equilibrium constant
\(T\)  Temperature
\(X^i\)  Mass fraction of component \(i\)

\(\phi\)  Porosity
\(\Delta t\)  Time step
\(c\)  Molar concentration
\(pH\)  Parameter for the acidity or basicity of an aqueous solution
\(x\)  Mole fraction
\(\gamma^i\)  Activity coefficient of component \(i\)
\([i]\)  Activity of component \(i\)
\(\mu\)  Fluid viscosity
\(\nabla p\)  Pressure gradient
$\phi_0$ Initial porosity

$\phi_{CaCO_3}$ Volume fraction of calcite

$\phi_{crit}$ Critical porosity at which $K=0$

$\rho$ Fluid density

$\tau_A$ Characteristic advection time

$\tau_R$ Characteristic reaction time

$\theta$ Coupling error estimator

$\Delta x$ Discretization length in x direction

$a_i$ Ion specific parameter according to Truesdell and Jones

$b_i$ Ion specific parameter according to Truesdell and Jones

$c_i$ Effective diameter of the ion

$k_1$ Kinetic dissolution rate constant of calcite

$k_2$ Kinetic dissolution rate constant of calcite

$m_0$ Standard molality = 1

$m_i$ Molality of component i

$n_i$ Number of molecules of component i

$n_{total}$ Number of molecules of all components

$p_w$ Pressure of brine

$q^i$ Source or sink term of component i

$tol$ Tolerance of time size control for the decoupled model

$X_{i,u}^{c_i}$ Mass fraction of master species $u$ in element $i$ in the chemistry subsystem

$X_{i,u}^{t_i}$ Mass fraction of master species $u$ in element $i$ in the transport subsystem
$z_i$ Charge of ion $i$
Author’s Statement

I hereby certify that I have prepared this master’s thesis independently, and that only those sources, aids and advisors that are noted herein have been used or consulted.

Signature __________________ Date ________________
1 Introduction and Motivation

1.1 CCS project

To reduce the greenhouse effect, carbon dioxide capture and storage (CCS) has been presented by the international Panel Climate Change (IPCC). CCS project consists of the separation of CO$_2$ from the sources, transport to the storage location and long term isolation from the atmosphere [19].

Due to the large storage capacity, deep saline aquifers are assumed as the potential storage. Because of the high risk of leakage, it is important to identify the underground behavior of CO$_2$ after injection. Since the complex geological and chemical conditions under the ground and the demands for the safe storage over a long time, it is necessary to build a conceptional model and simulate the reactive transport process of CO$_2$ in the storage reservoir.

1.2 Solution methods for highly complex system

The CO$_2$ dissolved in the brine phase combines with water to form carbonic acid (H$_2$CO$_3$), causing a decrease in the pH. It triggers the geochemical dissolution of the mineral calcite phase (CaCO$_3$) [17]. The dissolution of the mineral counteracts with a strong drop of pH, therefore the system is also called the buffered system.

Due to these reactions with the solid matrix, porosity and thereby permeability will be changed. The tight coupling between solute transport and porous media due to kinetic reactions results in a highly nonlinear system of partial differential algebraic equations. Two different approaches are presented here to solve this problem: (1) the fully coupled approach (FC) (2) the sequential non-iteration approach (SNIA), here referred to as the decoupled approach. The main difference of these two models depends on how to deal with the reaction term and transport equations.

Yeh and Tripathi compare the different approaches for two, three dimensions and conclude that the fully coupled model leads to excessive CPU memory and CPU time, due to large set of equations with increasing unknowns [27].
The drawback of SNIA is the introduction of splitting error or coupling error. SNIA has been analyzed in the case of a single species instantaneous adsorbed to the solid phase [13], where the absorption is modeled using a linear isotherm. It was presented that numerical diffusion, proportional to $\Delta t$, is induced by the coupling error. Another analysis of the errors introduced by operator splitting was based on the case of a radioactive decay process occurring simultaneously with advection and diffusion [23]. In this case the operator splitting again resulted in mass balance errors proportional to $\Delta t$. Therefore, time step need to be controlled to obtain accurate solution [4] and corresponding error estimator to adjust the time step is applied in simplified simulation of linear decay and single Michaelis-Menten kinetics [16][20].

For the case of kinetic dissolution behavior of calcite with a CO$_2$ rich water injection, the time scales of dynamic reactions and transport are quite different and the chemical reactions are only dependent on local species’ concentrations. Therefore, the operator-splitting approach is justified to be an efficient method to solve this problem.

A decoupled model has been implemented in the DuMx for the case of kinetic dissolution of calcite due to an acidic injection. The objective of this thesis is to investigate performance and accuracy of the implemented decoupled model in comparison to the fully coupled model [17] with respect to large simulation domains.

1.3 Structure of this thesis

In the following, an overview is given which shows the structure of this work.

In Chapter 2, fundamental definitions concerning for the physical properties of the porous media are explained in Section 2.1. The relevant concepts and laws for geochemistry are declared in Section 2.2.

In Chapter 3, mathematical formulations and numerical methods are presented for fully coupled and the decoupled model in detail. Mass balance equations and supplementary equations are applied for primary and secondary species respectively in Section 3.1 and 3.2. Subsequently, numerical discretization are explained for the both model in Section 3.3.

In Chapter 4, first the base problem is described in Section 4.1. Then, different maximum time step size for the coupled model are compared to validate with the existing coupled model [17] in Section 4.2. Different fixed tolerances for the time step size control are investigated to choose an efficient tolerance for the decoupled model in Section 4.3. In the end, accuracy and efficiency of the implemented decoupled model and fully coupled model are evaluated with increasing number of unknowns in Section 4.4.
In Chapter 5, conclusions are drawn from the results given in the Chapter 4.
2 Fundamentals

In this chapter, the physical properties of the porous media and the relevant definitions and laws for geochemistry are presented.

2.1 Physical properties

This section gives an overview of the basic physical property concerning the porous media, for more detailed information referred to [12]. In porous media flow models, a continuum approach is applied to average the micro scale properties over a representative elementary volume (REV) [25]. Parameters to describe the effects of the interaction of the fluid and solid matrix on this macro scale will be introduced.

2.1.1 Porosity

Porosity $\phi$ is employed to represent the ratio of void space to the total volume of the solid rock matrix at REV scale. It is defined as

$$\phi = \frac{V_{\text{pore}}}{V_{\text{total}}}, \quad (2.1)$$

where $V_{\text{pore}}$ is pore volume within the REV. $V_{\text{total}}$ is the total volume of the REV. Porosity shows a simplified average structure of a REV at a macro scale.

2.1.2 Intrinsic permeability

It is necessary to considering the interaction between fluid and the solid matrix in the porous media.

The concept of intrinsic permeability $K$ accounts for the influence of fluid viscosity and adhesion at the surface of the solid matrix in a macroscopic approach. It relates the potential gradients $\nabla p - \rho g$ with flow velocity for a given fluid viscosity $\mu$.

$$v = -\frac{K}{\mu}(\nabla p - \rho g), \quad (2.2)$$
Where $\mu$ is fluid viscosity, $\nabla p$ is the pressure gradient, $\rho$ is the density of fluid, and $g$ is the gravitational acceleration. Intrinsic permeability $K$ depends on the porosity and the spatial distribution and connectivity of the pores in the porous media.

2.2 Chemical properties

The following section focuses on some definitions of basic chemical terms and an overview of the different equations which are relevant to describe lime-carbonic acid balance. For more detailed information on groundwater chemistry refer to [1].

2.2.1 Concentration

The molar concentration $c$ is defined as

$$c \left[ \frac{mol}{m^3} \right] = \frac{\text{number of molecules}}{\text{volume}},$$

and mass concentration $C$ is defined as

$$C \left[ \frac{kg}{m^3} \right] = \frac{\text{mass of substance}}{\text{volume}}.$$

2.2.2 Mole and mass fraction

Mass fraction $X$ is defined as the ratio between the mass of one component and the total mass of all components. It can be written normally as

$$X \left[ \frac{kg}{kg} \right] = \frac{\text{mass of the substance}}{\text{total mass}},$$

Analogously the mole fraction $x$ is defined as

$$x \left[ \frac{mol}{mol} \right] = \frac{n_i}{n_{total}},$$

where $n_i$ is the number of molecules of component $i$ and $n_{total}$ is the number of molecules of all components.

2.2.3 Molality

Molality $m$ is defined as the ratio of the amount of solute in mol and the mass of solvent in kg.
2.2.4 Ionic strength

Ionic strength $I$ is used to describe the activity coefficients of the different ions. It is based on the molality $m_i$ and charge $z_i$ of each component $i$.

$$ I = \frac{1}{2} \sum_{i=1}^{n} \frac{m_i z_i^2}{m_0} = \frac{1}{2} (m_{\text{Na}^+} + m_{\text{Cl}^-}), $$

where $n$ is the number of different ions in the solution and $m_i$ is the molality of component $i$, $z_i$ is the charge of component $i$ and $m_0$ is the standard molality, $m_0 = 1$. In this work, ionic strength only depends on the molality of $\text{Na}^+$ and $\text{Cl}^-$.

2.2.5 Law of mass action

The law of mass action is a mathematical model to describe an equilibrium reaction. It shows for

$$ aA + bB \rightarrow cC + dD. $$

as

$$ \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_{eq} = \prod \gamma_i^{\nu_i}, $$

where $[A], [B], [C], [D]$ are the activities of the components $A, B, C, D$ and $a, b, c, d$ are their stoichiometric coefficients. $K_{eq}$ is the equilibrium constant, $c_i$ is the concentration of component $i$ and $\nu_i$ is its stoichiometric coefficient. In a real reaction system the law of mass action should be considered including activity coefficient. Equation 2.10 can be rewritten as

$$ K_{eq} = \prod \gamma_i^{\nu_i}. $$

2.2.6 Activity and activity coefficient

Activity describes the effect that there are interactions between different ions due to Coulomb forces, which make some ions less active to participate in reactions. It is necessary to define a dimensionless concentration called activity to adjust the molar concentration to the real system. The activity $[i]$ is quantified for each component $i$ by the activity coefficient $\gamma_i^A$ of component $i$ and the molality $m_i$.  

$$ m \left[ \frac{mol}{kgH_2O} \right] = \frac{\text{amount of solute(mol)}}{\text{mass of solvent(kg)}}. $$
Figure 2.1: Relationship between activity coefficients $\gamma^i$ and the ionic strength $I$ for the extended Debye – Hückel equation [17].

$$[i] = \gamma^i \frac{m_i}{m_0}.$$  \hspace{1cm} (2.12)

The most common empirical equation for calculating the activity is the *debye–Hückel* equation [1], in which the ionic strength $I$ is closely related to the activity coefficient $\gamma^i$. The *debye–Hückel* equation can be written as

$$\log \gamma^i = -\frac{A z_i^2 \sqrt{I}}{1 + B c_i \sqrt{I}},$$  \hspace{1cm} (2.13)

Where $A$ and $B$ are parameters defined in Table 4.4 and $c_i$ is the effective diameter of the ion. This equation is only valid for ionic strength below 0.1. An extended version of the *Debye – Hückel* equation, for salinities up to 2, is available according to [1].

$$\log \gamma^i = -\frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I,$$  \hspace{1cm} (2.14)

Where $a_i$ and $b_i$ are ion specific fit parameters listed in Table 4.3. Due to the term $b_i I$, which is independent from the charge, the activity of uncharged species can be calculated, for example dissolved gases like CO$_2$. The relationship between activity coefficients for some relevant species and the ionic strength $I$ are plotted in Fig 2.1.

The equation can be extended to *Pitzer* equations [21], which is used to calculate activities for solutions with high ionic strength.
2.2.7 pH

The pH is a parameter describing the acidity or basicity of an aqueous solution. It is defined as the negative common logarithm of the activity of H\(^+\) ions.

\[
pH = -\log([H^+]),
\]

(2.15)

where \([H^+]\) is the activity of hydrogen ion.

2.2.8 Salinity

Salinity describes the cumulated effect of the dissolved ions on the density of the solution and the ionic strength. In this work, the salinity of the brine is calculated as the sum of the mass fraction of Na\(^+\) and Cl\(^-\).

\[
\text{Salinity} = \frac{\text{mass of dissolved ions}}{\text{mass of water}}.
\]

(2.16)

\[
X^{\text{sal}} = X^{\text{Na}^+} + X^{\text{Cl}^-},
\]

(2.17)

where \(X^{\text{sal}}\) is the salinity of the brine, \(X^{\text{Na}^+}\) is the mass fraction of Na\(^+\), \(X^{\text{Cl}^-}\) is the mass fraction of Cl\(^-\).

2.2.9 Dissociation of water

Dissociation of water is to be described:

\[
H_2O \rightleftharpoons H^+ + OH^-.
\]

(2.18)

\[
K_w = \frac{[OH^-][H^+]}{[H_2O]},
\]

(2.19)

Where \(K_w\) is the dissociation constant for H\(_2\)O.

2.2.10 Dissociation of carbonic acid and bicarbonate

Deep brine aquifers are not directly contact with any fresh recharge water and the salinity of brine ranges from 5000 to > 350000 mg/L [11]. If the CO\(_2\) is injected into the aquifer, the environment is altered by dissolved CO\(_2\) that reacts with water to form carbonic acid (H\(_2\)CO\(_3\)).
$CO_2 + H_2O \rightleftharpoons H_2CO_3$. \hspace{1cm} (2.20)

Carbonic acid is a weak acid that dissociates into bicarbonate and hydrogen ions. Bicarbonate further dissociates forming carbonate:

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$. \hspace{1cm} (2.21)

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$. \hspace{1cm} (2.22)

For the dissociate of carbonic acid and bicarbonate is much faster than the dissolution of calcite. It is assumed that chemical equilibrium occurs instantaneously. Consequently, the equilibrium coefficients $K_1$ and $K_2$ will be applied for the law of mass action according to Eq (2.21-2.22).

$$K_1 = \frac{[HCO_3^-][H^+]}{[CO_2]} \hspace{1cm} (2.23)$$

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \hspace{1cm} (2.24)$$

2.2.11 Calcite dissolution

The presence of $H^+$ due to the carbonic acid results in dissolution of calcite $CaCO_3$. Dissolution process of calcite can be described by the following two reactions.

$CaCO_3(s) + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$. \hspace{1cm} (2.25)

$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^-$. \hspace{1cm} (2.26)

$$K_{CaCO_3} = \frac{[CO_3^{2-}][Ca^{2+}]}{[CaCO_3]} \hspace{1cm} (2.27)$$

Dissolution of calcite consumes the hydrogen ion, which counteracts the decrease of pH due to the dissolution of carbonic acid. The existence of $HCO_3^-$ and $CO_3^-$ prevents the pH of the whole system drop severely.
Calcite solubility product $K_{\text{CaCO}_3}$ is defined as equation (2.27). Saturation state of calcite $\Omega$ is described by the activities $[\text{CO}_3^{2-}], [\text{Ca}^{2+}]$ and calcite solubility product $K_{\text{CaCO}_3}$.

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{CaCO}_3}}.$$ (2.28)

The equilibrium state $\Omega = 1$, where the rates of precipitation and dissolution are equal, is reached. The rate of kinetic dissolution of calcite is dependent on the calcite saturation state $\Omega$.

**2.2.12 Damköhler number**

A system of reactive components is said to be in a state of equilibrium if the chemical potential of the system is zero. A state of equilibrium is the state where the rate of construction is equal to its rate of destruction. Every system strives towards a state of equilibrium in order to maximize its entropy. However, the time for an equilibrium to be established varies and depends on the type of reactions involved.

The Damköhler number $D$ is a dimensionless number to relate the characteristic advection time $\tau_A$ to the chemical reaction time $\tau_R$.

$$D = \frac{\tau_A}{\tau_R} = \frac{\Delta x}{v \tau_R},$$ (2.29)

where $\Delta x$ is the discretization length in $x$ direction, $v$ is the specific flux of the fluid. For $\tau_A \gg \tau_R$ the system can be assumed to be in a state of equilibrium. In other words, when different components are transported through a water-saturated porous medium, front development occurs over a short distance and system is under local chemical equilibrium. For $\tau_A \ll \tau_R$, front development changes over a longer distance and a kinetic approach has to be considered [17].
3 Mathematical Modelling and Discretisations

In this chapter, the mass balance equations are presented in the first section, completed by supplementary equations to describe the chemical reaction. Afterwards, overviews over the numerical schemes for the fully coupled model and decoupled model are given.

Generally, when setting up a system of transport reactive equations there is a differentiation between master species and secondary species [18]. The master and secondary species are used to simulate the base problem listed in the Table 3.2.

Mass balance equations only need to be solved for the master species, since the secondary variables can then be derived through the supplementary equations.

Eleven components (H$_2$O, C$_{tot}$, Na$^+$, Cl$^-$, Ca$^{2+}$, CaCO$_3$, H$^+$, OH$^-$, CO$_2$, HCO$_3^-$, CO$_3^{2-}$) for the simulation of the base problem are required with linearly independent master species (H$_2$O, C$_{tot}$, Ca$^{2+}$, Na$^+$, Cl$^-$ and CaCO$_3$). With C$_{tot}$ and Ca$^{2+}$ as master species it is possible to determine the secondary species by the supplementary equations. H$_2$O, Na$^+$ and Cl$^-$ are not directly needed for the calculation of the chemical reactions, since the activity of H$_2$O is assumed to be one and Na$^+$ and Cl$^-$ are not taking part in the reactions. However, their concentration is needed for the calculation of ionic strength Eq (2.8), which is necessary to acquire the activity coefficient of component.

Therefore, eleven equations are required to solve all unknowns [17]. Six equations are derived for the master species from the mass balance of five mobile species and calcite mineral Eq (3.1-3.2). In addition, due to the dissolution of calcite the variable porosity and permeability are considered Eq (3.11-3.12). Other equations as the supplementary equations are solved for the secondary species. Three equations 2.23, 2.24 and 2.19 will be applied for considering that the dissociation reactions are in a state of equilibrium. The total carbon equation and charge balance equation are also used Eq (3.6- 3.7).

3.1 Mass balance equations

In this section, the mass balance equations are divided into two parts, transport part and source or sink terms due to reactions [15]. Six equations are described for the mass
Table 3.1: Primary and secondary species for the base problem simulation [17].

<table>
<thead>
<tr>
<th>primary species</th>
<th>H_2O, C_{tot}, Na^+, Cl^−, Ca^{2+}, CaCO_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>secondary species</td>
<td>H^+, OH^−, CO_2, HCO_3^−, CO_3^{2−}</td>
</tr>
</tbody>
</table>

balance of mobile species and the calcite phase as the primary species.

### 3.1.1 Transport equations

The base problem will be simplified as one phase reactive transport processes with multiple components included solid mineral.

\[
\frac{\partial (\phi X_i \rho)}{\partial t} - \nabla \left\{ \rho X_i \frac{K}{\mu} (\nabla p_w - \rho g) \right\} - \nabla \left\{ D_{pm} \rho \nabla X_i \right\} = q_i, \quad (3.1)
\]

where \( \phi \) is the porosity, which is changed due to chemical reaction and defined in subsection 3.2.2 Eq (3.11). \( X_i \) stands for the mass fraction of component \( i \), \( \rho \) is the fluid density, \( p_w \) is the pressure of brine, \( \mu \) is the phase viscosity. \( K \) is the permeability tensor, which due to the changed porosity is variable and is described in subsection 3.2.2 Eq (3.12). \( g \) is the gravity vector. \( D_{pm} \) is the diffusion coefficient within the porous medium. \( q_i \) is the source or sink term of component \( i \).

- **Mass Balance of CaCO_3**:

\[
\frac{\partial (\phi_{CaCO_3} \rho_{CaCO_3})}{\partial t} = q^{CaCO_3} \quad (3.2)
\]

Where \( \phi_{CaCO_3} \) is the volume fraction of calcite, \( \rho_{CaCO_3} \) is the mineral density of calcite. \( q^{CaCO_3} \) is the source term of calcite defined in Eq (3.4).

### 3.1.2 Source and sink terms due to reactions

At the right side of the mass balance equation, source or sink terms are to describe the increase or decrease by the unit of the molar rate of each component. In this subsection, the source or sink term are given in the following.

- **H_2O, Na^+, Cl^−**

The source terms for H_2O, Na^+, Cl^− equal zero, for none of them are involved in the reactions.
\[ q_{\text{H}_2\text{O}} = q_{\text{Na}^+} = q_{\text{Cl}^-} = 0 \]  

(3.3)

- **Calcite CaCO\(_3\)**

For calcite, the source term \( q_{\text{CaCO}_3} \) is dependent on the dissolution or precipitation.

The rate of calcite precipitation or dissolution is based on the saturation state \( \Omega \) Eq (2.28). When \( \Omega < 1 \), dissolution occurs and the kinetic rate is calculated in the following.

\[ q_{\text{CaCO}_3} = \{ k_1 [\text{H}^+] + k_2 \} \{ 1 - \Omega \}, \]

(3.4)

where \( k_1, k_2 \) are kinetic rate constants listed in Table 4.1 for the simulation of the base problem [8][2].

- **Ca\(^{2+}\), C\(_{\text{tot}}\)**

\[ q_{\text{Ca}^{2+}} = q_{\text{C}_{\text{tot}}} = -q_{\text{CaCO}_3} \]  

(3.5)

The source terms of the molar rate of Ca\(^{2+}\) and C\(_{\text{tot}}\) have the negative sign of the source term of CaCO\(_3\).

### 3.2 Supplementary equations

Not only the primary species need to be defined, but mass fractions of the different secondary species, properties of the porous medium, properties of the brine also need to be calculated.

#### 3.2.1 Mass fractions of the secondary species

- **Total Carbon Equation:**

\[ m_{\text{C}_{\text{tot}}} = m_{\text{CO}_2} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} \]

(3.6)

where \( m_{\text{C}_{\text{tot}}} \) is the molality of the total carbon, \( m_{\text{CO}_2} \) is the molality of CO\(_2\), \( m_{\text{HCO}_3^-} \) is the molality of HCO\(_3^-\), \( m_{\text{CO}_3^{2-}} \) is the molality of CO\(_3^{2-}\), C\(_{\text{tot}}\) as the master species is related with relevant secondary species HCO\(_3^-\), CO\(_3^{2-}\), CO\(_2\) in this equation.
• Electro Neutrality Equation:

\[ m_{H^+} + 2m_{Ca^{2+}} = m_{OH^-} + m_{HCO_3^-} + 2m_{CO_3^{2-}} \]  

(3.7)

The electro neutrality has to be guaranteed that the entire system has no electric charge. So the sum of all products of the charge \( z_i \) and the molality \( m_i \) of each component \( i \) has to be equal to zero.

• Equilibrium \( H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \) Eq (2.21)

\[ K_1 = \frac{[HCO_3^-][H^+]}{[CO_2]} \]  

(3.8)

• Equilibrium \( HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \) Eq (2.22)

\[ K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \]  

(3.9)

• Equilibrium \( H_2O \rightleftharpoons H^+ + OH^- \) Eq (2.18)

\[ K_w = \frac{[OH^-][H^+]}{[H_2O]} \]  

(3.10)

According to the law of mass action, the equilibrium reaction can be expressed as equations (3.8-3.10). Activity of relevant components will be applied in these three equations. First, ionic strength \( I \) can be calculated from molality of \( Na^+ \) and \( Cl^- \) Eq (2.8). Afterwards, according to the extended version of the Debye – Hückel equation Eq (2.14) activity coefficients \( \gamma^i \) are obtained. Figure 3.1 shows the sequence for calculating the activity \( \gamma^i \). Therefore, secondary species will be expressed with respect to \( C_{tot} \) and \( H^+ \) by using supplementary equations in the Newton loop. Constants for equilibrium reactions are given in Table 4.2.

### 3.2.2 Properties of the porous medium

The dissolution of the calcite will increase the porosity of the porous medium. The changed porosity \( \phi \) can be calculated from the volume fraction of calcite \( \phi_{CaCO_3} \) and the initial porosity \( \phi_0 \)

\[ \phi = \phi_0 - \phi_{CaCO_3} \]  

(3.11)

The permeability will increase when more space is available for the fluid flow due to changing porosity. The permeability is calculated by the Kozeny-Carmantype relation [26][15].
Figure 3.1: Variables calculated for the activity of component $i$. 

- Molality of sodium ion
- Molality of chloride ion
- Ionic strength $I$ of component $i$
- Activity coefficient of component $i$
- Molality of component $i$
- Activity $[i]$
Table 3.2: Secondary variables calculated from the primary variables [15].

<table>
<thead>
<tr>
<th>Properties of the brine</th>
<th>Variables needed</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density brine</td>
<td>$\rho$</td>
<td>$p, T, X^{\text{sal}}, X^{\text{CO}_2}$ Batzle and Wang [24].</td>
</tr>
<tr>
<td>Viscosity brine</td>
<td>$\mu$</td>
<td>$p, T, X^{\text{sal}}, X^{\text{CO}_2}$ Batzle and Wang [24].</td>
</tr>
<tr>
<td>Salinity</td>
<td>$X^{\text{sal}}$</td>
<td>$X^{\text{Na}^+}, X^{\text{Cl}^-}$ $X^{\text{sal}} = X^{\text{Na}^+} + X^{\text{Cl}^-}$ Eq (2.17)</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>$I$</td>
<td>$X^{\text{Na}^+}, X^{\text{Cl}^-}$ $I = \frac{1}{2}(m_{\text{Na}^+} + m_{\text{Cl}^-})$ Eq (2.8)</td>
</tr>
</tbody>
</table>

$$K = K_0 \left( \frac{\phi - \phi_{\text{crit}}}{\phi_0 - \phi_{\text{crit}}} \right)^3 \text{ if } \phi > \phi_{\text{crit}}; \text{ else } K = 0,$$

(3.12)

where $K_0$ is the initial permeability, $\phi_{\text{crit}}$ is the critical porosity, when the permeability is zero.

3.2.3 Properties of the brine

The salinity of the brine is calculated as the sum of the mass fraction of $\text{Na}^+$ and $\text{Cl}^-$ Eq (2.17). In addition, ionic strength also can be obtained by modality of $\text{Na}^+$ and $\text{Cl}^-$ Eq (2.8). Using salinity, Temperature $T$, and pressure of the liquid $p$, the density can be calculated according to Batzle and Wang [24]. The properties of the brine are evaluated from the the primary variables are shown in Table 3.2.

3.3 Numerical discretisation

The system of equations which has to be solved is a system of coupled, highly non-linear partial differential equations. These equations will be solved in the numerical method. Thus the equations shown in section 3.1 and 3.2 have to be discretized in time and space. This is done for both models by using the numerical simulator DuMx$^*$ [10].

3.3.1 Spatial discretisation

The BOX method is used for spatial discretization for the coupled and the decoupled model. The BOX method is a combination of the finite volume and the finite element method. The box $B_i$ consist of different sub control volumes (SCV) of the elements of which the node $i$ is a part. To construct those sub control volumes, the barycenter of each element is connected to the point in the center of node $i$ and its adjacent nodes $j, k, l, m, n, o, p$. On the surface of the SCV, the integration points (IPs) are defined as the middle between the barycenter and the center between node $i$ and its neighboring
Figure 3.2: Spectrogram of the different solution steps inside a time step [17].
Figure 3.3: Unstructured 2D BOX mesh [6].

nodes. The fluxes are calculated by multiplying the flow velocity at the IPs with the cross-sectional area of the corresponding SCV face. The value of the primary variables at the IPs is estimated with interpolating function used in the finite element method. Figure 3.3 shows the structure of a BOX mesh. Advantage of the BOX method are the conservation of mass due to the use of a finite volume-like scheme to evaluate the fluxes. For detailed information about the box method, see [6][15].

Since the base problem to be simulated is advection dominated, in order to increase the stability, a fully upwind method is used to calculate fluid properties like density or viscosity dependent on the upstream node [15]. However, the front will also be smeared out for using this method [12].

3.3.2 Time discretisation

A fully implicit Euler scheme is applied for the coupled model, in which the coupled system of equations will be solved in an iterative approach. The mass balance equation for five mobile species Eq (3.1) and solid calcite phase Eq (3.2) will be expressed as:

$$\frac{\partial x}{\partial t} \approx \frac{x^{i+1} - x^i}{t_{i+1} - t_i} = A^{i+1}x^{i+1}, \quad (3.13)$$

where $x^{i+1}$ is the vector of primary variables at the new time level $t_{i+1}$, $x^i$ is the vector of primary variables at the previous time level $t_i$ and $A^{i+1}$ is a matrix with coefficients depending on the primary variables at the new time level [17]. Primary variables are
The fully implicit scheme has the advantage of being unconditionally stable, so there is no time step size constraint in order to ensure stability [12]. However, the local truncation error in the discretization method primarily depends on the time-step size $h$ [22][14][5], which is varied among the solution in order to minimize the computational effort subject to a prescribed accuracy requirement. Time discretization will be described in detail for the decoupled model in subsection 3.3.4.

### 3.3.3 Solution method of the fully coupled model

The nonlinear system of equations is solved by the iterative Newton method and a spectrogram of the solution is given in Figure 3.2 [17].

An automatic time stepping method is applied to the fully coupled model and the time step size depends on the speed of convergence of the last Newton step and the maximum step size limitation. The outer Newton loop is first initialized using the last step solution. For every time step an outer loop has to be solved for the mass balance equations of the master species Eq (3.1-3.2). In every step the composition of brine and the secondary variables have to be determined as functions of the primary variables of the last time step. The Jacobian matrix $J$ and the residual $R$ are set up using the primary and secondary variables and the resulting linear system of equations

\[
J \left( x^{t+1,n+1}_i \right) u = J \left( x^{t+1,n+1}_i \right)
\]

is solved, where $n$ is the iteration step, $u = x^{t+1,n+1}_i - x^{t+1,n}_i$ and $x^{t+1,n+1}_i$ and $x^{t+1,n}_i$ are the vectors of unknowns at the time step $t_{i+1}$ and the iteration steps $n+1$ and $n$ respectively. A relative criterion has to be fulfilled for convergence of each Newton loop. Initializing of the loop is done by using solutions of the previous time or Newton step. Primary variables and secondary variables are listed in Table 3.1.

A second Newton–Rapson solver is used in an inner Newton loop to obtain the secondary variables. The primary variable $C_{\text{tot}}$ are known from the outer loop and all the secondary variables will be solved by expressing with respect to $C_{\text{tot}}$ and $H^+$ by using equations for dissociation of carbonic acid, bicarbonate and water Eq (3.8,3.9,3.10), the
Figure 3.4: An illustration of the solution method for the decoupled model.

carbon balance equation Eq (3.6) and charge balance equation Eq (3.7).

3.3.4 Solution method of the decoupled model

The basic idea of the decoupled model is to split out the chemistry parts from the mass balance equations such that the chemistry parts and the transport parts can be solved separately with different numerical techniques and time steps. The decoupled method substantially enhances computational efficiencies by setting the source or sink term to be zero in the transport subsystem. For each step transport and chemistry subsystem will be solved in their own steps, it is especially suited for the system of coupled nonlinear partial differential equations related with mass transport and kinetic chemistry whose time scale are quite far apart.

The decoupled formulation can be implemented in many ways. For example, the transport subsystem can be solved by any convenient numerical techniques, such as particle tracking, finite differences [3]. In this work the transport step is solved as a fully coupled model, but without source or sink term at the right hand and the subsystem
will be divided into many small time steps by using Newton method until it finishes this whole time step. Afterwards computed solution from the transport subproblem as the initial condition will be used for calculating the kinetic calcite dissolution rate Eq (3.4) from the beginning of this time step of the whole system. Then corresponding mineral variable, secondary variables are sequentially calculated in chemistry subsystem. At the same time, relevant primary variables will be changed due to the reaction. Finally, the solution of the chemistry subsystem is regarded as the solution of the whole system for this step. As is expected, the time step of the whole system could not be divided too large to avoid causing big error. The difference of the primary variables between the two subproblems can be applied as the indicator to control the following time step size.

It is also noticed that time discretization of transport subsystem is implicit method, but it can not ensure the whole system will be stable. It is necessary to choose the reasonable time step size to avoid oscillation in the decoupled model. An adaptive time step control attempt to ensure a stable distribution of errors over the whole simulation time. An initial time step and a fixed tolerance are chosen. Then, the following time step size is based on the coupling error indicator $\theta$.

$$\theta = \min \left( \frac{t_{tol}}{E_c}, 2 \right).$$  \hspace{1cm} (3.15)

$$\text{nextstep size} = \text{laststep size} \cdot \theta.$$ \hspace{1cm} (3.16)

In this equation, 2 is a safety factor which avoids too large value for the next step, $t_{tol}$ is the chosen fixed tolerance, $E_c$ is the coupling error described by the following equation Eq (3.17). It can be seen the higher the tolerance is, the bigger the coupling error indicator it is. Consequently, the next time step size will be increased fast. On the contrary, lower tolerance results in smaller time step size but ensure more stable solution. Therefore, it is necessary to choose an efficient tolerance for the decoupled model.

Coupling error or splitting error is to describe the maximum difference of the transport and chemical subsystem for the master species over all elements for every time step of the whole system.

$$E_c = \max \left( \frac{X^{t,u}_i - X^{t,u}_c}{\frac{X^{t,u}_i + X^{t,u}_c}{2}} \right),$$ \hspace{1cm} (3.17)

*i.e.* all the elements, $u \in \{\text{H}_2\text{O}, \text{C}_{\text{tot}}, \text{Ca}^{2+}, \text{Na}^+, \text{Cl}^-\}$

Where $X^{t,u}_i$ is the mass fraction of master species $u$ in each element $i$ in the transport
subsystem, $X_{c}^{i,u}$ is the mass fraction of the same master species $u$ of element $i$ in the chemistry subsystem.

Spatial discretization of transport and chemistry is identical, so that it can exchange information directly between master variables in transport and chemistry subsystems.
4 Comparison Studies

In this chapter, first a base problem is set up for both models. To compare these two different models described in the previous chapter, different maximum time step sizes are compared for the coupled model to validate with the existing coupled model [17]. Then, different tolerances are investigated for the implemented decoupled model to choose the tolerance for the time step size control to ensure the decoupled model is both accurate and efficient. Finally, the implemented decoupled model and the validated coupled model are compared in terms of accuracy and performance with increasing grid resolution.

4.1 Base Problem

The problem simulates the kinetic dissolution behavior of calcite caused by CO_2 rich water injection.

As depicted in Figure 4.1, the domain is comprised of a 1D column with a Neumann boundary at the right side, where CO_2 rich water is injected into the domain for a period of 25 days. The left side is a Dirichlet boundary condition.

The initial pH of the column is about 6.3. The water injected at the left side has a saturated total carbon concentration. However, the injected concentration of Ca^{2+} is zero, resulting in the strong state of calcite CaCO_3 dissolution. Dissociation constants are given in Table 4.2. The relevant parameters given in Table 4.3 and 4.4 are calculated for the activity of species according to the extended Debye − Hückel formulation [7].

k_1, k_2 are constants to calculate kinetic dissolution rate for calcite Eq (3.4) and other parameters are presented in Table 4.1.

4.2 Comparison of different time step size for the coupled model

The objective of this thesis is to compare the existing coupled model [17] to the decoupled model. First, it is necessary to validate the existing coupled model with the coupled model applied in this work.
Table 4.1: Parameters for the base problem [17].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial permeability $K_0$</td>
<td>$1e-13$</td>
<td>$[m^2]$</td>
</tr>
<tr>
<td>initial porosity $\phi_0$</td>
<td>0.15</td>
<td>$[-]$</td>
</tr>
<tr>
<td>initial density $\rho_0$</td>
<td>1087</td>
<td>$[kg/m^3]$</td>
</tr>
<tr>
<td>initial calcite porosity $\phi_{CaCO_3}$</td>
<td>0.1</td>
<td>$[-]$</td>
</tr>
<tr>
<td>initial $C_{tot}$ mole fraction</td>
<td>0.0008524349</td>
<td>$[-]$</td>
</tr>
<tr>
<td>initial $Na^+$ mole fraction</td>
<td>0.0323217443</td>
<td>$[-]$</td>
</tr>
<tr>
<td>initial $Cl^-$ mole fraction</td>
<td>0.0320886477</td>
<td>$[-]$</td>
</tr>
<tr>
<td>initial $Ca^{2+}$ mole fraction</td>
<td>0.0001456872</td>
<td>$[-]$</td>
</tr>
<tr>
<td>initial pressure $p_0$</td>
<td>8.0</td>
<td>$[MPa]$</td>
</tr>
<tr>
<td>initial water saturation</td>
<td>1</td>
<td>$[-]$</td>
</tr>
<tr>
<td>injected water</td>
<td>0.0012</td>
<td>$[kg/m^2s]$</td>
</tr>
<tr>
<td>injected CO$_2$ mass fraction</td>
<td>0.03</td>
<td>$[-]$</td>
</tr>
<tr>
<td>injected salinity mass fraction $X_{sal}$</td>
<td>0.1</td>
<td>$[-]$</td>
</tr>
<tr>
<td>kinetic rate constant $k_1$</td>
<td>8.9e-1</td>
<td>$[mol/m^3s]$</td>
</tr>
<tr>
<td>kinetic rate constant $k_2$</td>
<td>6.5e-7</td>
<td>$[mol/m^3s]$</td>
</tr>
<tr>
<td>temperature</td>
<td>25</td>
<td>$[{^\circ}C]$</td>
</tr>
</tbody>
</table>
### Table 4.2: Equilibrium constants at $T=25^\circ C$ [17]

<table>
<thead>
<tr>
<th>EQUILIBRIUM CONSTANT</th>
<th>VALUE</th>
<th>UNIT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_1$ for Eq (3.8)</td>
<td>6.3</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$pK_2$ for Eq (3.9)</td>
<td>10.3</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$pK_{\text{CaCO}_3}$ for Eq (2.28)</td>
<td>8.3</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$pK_w$ for Eq (3.10)</td>
<td>14</td>
<td>$[-]$</td>
</tr>
</tbody>
</table>

### Table 4.3: Ion specific fit parameters for the extended Debye–Hückel Equation at $T=25^\circ C$ [17].

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>$a/(10^{-10}m)$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>5.0</td>
<td>0.165</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>5.4</td>
<td>0.0</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>5.4</td>
<td>0.0</td>
</tr>
<tr>
<td>H$^+$</td>
<td>4.78</td>
<td>0.24</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>10.65</td>
<td>0.21</td>
</tr>
</tbody>
</table>

The implicit method allows larger time step sizes with respect to the stability, but in order to achieve required accuracy, it is necessary to choose a reasonable maximum step size to fit with the existing coupled model.

The results of the coupled model using different maximum time step size limitations are compared with grid resolution ($\Delta x = 1m$, $\Delta y = 2m$) in Table 4.5.

#### 4.2.1 Results and discussion

Results of the coupled model with the different maximum time step sizes is given in Figure 4.2 and the corresponding CPU time is presented in Figure 4.3 and in Table 4.5.

It is shown in Figure 4.2 that the local truncation error of the coupled model with no limitation of time step size is quite large so that the profile is too smooth and the front travels fast. It is also a consequence of numerical diffusion.

It is also noticed in Figure 4.4 that the coupled model with a maximum time step of 2080 seconds has the best agreement with the existing coupled model [17]. Therefore, the coupled model with a maximum time step of 2080 seconds will be used as the coupled model.

### Table 4.4: Parameters for the extended Debye–Hückel Equation at $T=25^\circ C$ [17].

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.5085</td>
</tr>
<tr>
<td>$B$</td>
<td>$0.3285 \times 10^{10} \frac{1}{m}$</td>
</tr>
</tbody>
</table>
Table 4.5: Maximum step size and CPU time for the coupled model.

<table>
<thead>
<tr>
<th>model</th>
<th>maximum time step size (second)</th>
<th>CPU (second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2080</td>
<td>9570</td>
</tr>
<tr>
<td>2</td>
<td>4080</td>
<td>4769</td>
</tr>
<tr>
<td>3</td>
<td>5080</td>
<td>3541</td>
</tr>
<tr>
<td>4</td>
<td>9080</td>
<td>1840</td>
</tr>
<tr>
<td>5</td>
<td>19080</td>
<td>1119</td>
</tr>
<tr>
<td>6</td>
<td>with no limitation</td>
<td>739</td>
</tr>
</tbody>
</table>

Figure 4.2: a)-c) Results of different maximum time step sizes for the coupled model. a) $C_{tot}$, b) pH, c) $Ca^{2+}$. 
Figure 4.3: CPU time of different maximum step sizes for the coupled model.

reference model to be compared with the decoupled model.

However, as is shown in Figure 4.2, too small time steps will cost CPU time but could not improve the accuracy much. Consequently, a maximum time step size of 5080 seconds is applied for the comparison of increasing grid resolution in section 4.4.

4.3 Comparison of time step control of using different tolerances for the decoupled model

As a test for the time step control for the decoupled model, the decoupled model using different tolerances is compared to the fully coupled reference model with the same grid resolution (grid 100 1).

4.3.1 Results and discussion

First, Figure 4.5 a)-d) compare the evolution of $C_{\text{tot}}$, pH, $\Omega$, and $\text{Ca}^{2+}$ after 25 days of injection between using different tolerances of the decoupled model to the validated fully coupled model.

As is shown in Figure 4.5 a) the front of $C_{\text{tot}}$ is around 50m. However, the profile of $\Omega$, which is to estimate the saturation state of calcite, is much different. Equilibrium state ($\Omega = 1$) is reached at a distance of about 25 m from the injection point, which means the kinetic dissolution rate for calcite is much slower than the transport front velocity so that
Figure 4.4: a)-c) Validation of the existing model [17] with the coupled model applied in this work with the maximum time step size of 2080 seconds. a) $C_{\text{tot}}$, b) pH, c) $\text{Ca}^{2+}$.
Figure 4.5: a)-d) Results of the decoupled model using different tolerances. a) C\text{tot}, b) pH, c) Ω, d) Ca\textsuperscript{2+}. 
the front of the highest dissolved concentration of $\text{Ca}^{2+}$ is approximately 25m behind the front of $\text{CO}_2$ rich water. Besides, there is also a slight decrease at about 50 m, which can be expected as a non-equilibrium state at that point for the mixing of acidified and non-acidified water. This can be illustrated with the help of Tillmans's curve [9][17].

The difference of time scale of transport and reaction processes give the possibility to using the decoupled model where the transport and reaction solver adjust their own steps size individually.

The overall behavior of the decoupled model is much similar to the fully coupled reference model, except for the decoupled model using the tolerance of $10^{-3}$. It is shown in Figure 4.7 a) that due to coupling error the profiles of mass fraction of calcium ion for the decoupled model using different tolerances could not fit each other at the injection point, where the highest kinetic dissolution rate is observed. The profile of $\text{Ca}^{2+}$ for the decoupled model using tolerance of $10^{-5}$ has the best agreement with the coupled model. Contrarily, larger coupling error cause oscillation at the injection point for the decoupled model using tolerance of $10^{-3}$. The smaller the tolerance is, the lower mass fraction of $\text{Ca}^{2+}$ at the injection point will reach. The different value of $\text{Ca}^{2+}$ at the injection point can be expected due to the influence of the coupling error. It can be observed that decreasing the tolerance of the decoupled model can improve the accuracy of the solution for the decoupled model.

Differences for using different tolerances are also found at the front in Figure 4.9. The higher the coupling error is, the larger mass fraction of $\text{Ca}^{2+}$ is transported at the front, except for the tolerance of $10^{-3}$. With the decrease of coupling error, the profile of the decoupled model is in good agreement with the coupled model.

The profiles of volume fraction of calcite close to the injection point for the decoupled and the fully coupled model are shown in Figure 4.8. The reduction of volume of calcite at the injection point for the reference coupled model is the strongest among all the models. Because the constant injection will lead the strong unsaturated state of $\text{Ca}^{2+}$ and thereby calcite phase at the injection point has the highest dissolution rate. As can be seen in Figure 4.7 a) at the injection point, the mass fraction of $\text{Ca}^{2+}$ is the lowest and reaches a constant state for the reference model. The larger coupling error the decoupled model has, the higher the mass fraction of $\text{Ca}^{2+}$ occurs at the injection point. Consequently, less calcite is dissolved at the injection point for the decoupled model than the fully coupled model.

Since it is also noticed that after 10m, the volume fraction of calcite is not much changed in Figure 4.8, it is shown in Figure 4.10 how the volume fraction of calcite is developed for points ($0m \leq x \leq 5m$) during the simulation time for the decoupled model.
Figure 4.6: a)-d) Temporal development of the saturation state of calcite $\Omega$ for the decoupled model using different tolerances. a) $x=0\,\text{m}$, b) $x=5\,\text{m}$, c) $x=15\,\text{m}$, d) $x=20\,\text{m}$.
Figure 4.7: a)-d) Temporal development of Ca$^{2+}$ for the decoupled model using different tolerances. a) $x=0$ m, b) $x=5$ m, c) $x=15$ m, d) $x=20$ m.
Figure 4.8: Volume of calcite after 25 days near the injection point for the decoupled model using different tolerances and the reference model.

Figure 4.9: Front of calcium ion for the decoupled model using different tolerances and the coupled reference model.
Figure 4.10: a)-c) Temporal development of volume of calcite for the decoupled model using different tolerances. a) x=0m, b) x=3m, c) x=5m.
Table 4.6: CPU time for the decoupled model using different tolerances.

<table>
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<th>total steps</th>
<th>average time size (second)</th>
<th>CPU Time (second)</th>
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<td>15</td>
<td>173334</td>
<td>244</td>
</tr>
<tr>
<td>5e-4</td>
<td>18</td>
<td>144444</td>
<td>364</td>
</tr>
<tr>
<td>1e-4</td>
<td>90</td>
<td>28889</td>
<td>895</td>
</tr>
<tr>
<td>8e-5</td>
<td>113</td>
<td>23009</td>
<td>1427</td>
</tr>
<tr>
<td>5e-5</td>
<td>185</td>
<td>14054</td>
<td>2316</td>
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<tr>
<td>1e-5</td>
<td>920</td>
<td>2826</td>
<td>9574</td>
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</tbody>
</table>

Because the overall behavior of the decoupled model using the tolerance of $10^{-3}$ is much different than other decoupled model, here it is taken a closer look at how the large coupling error influences on the results. It is shown in Figure 4.10 a) that at x=0m the volume fraction of calcite is much less reduced, while x=3m to x=5m the volume fraction of calcite is more reduced at the beginning. In addition, it is shown in Figure 4.6 c)-d) that the $\Omega$ value is decreased more at x=15m and x=20m at first, then, the profile rebound to higher value than other models. This can be expected because the accepted coupling error results in a front traveling further and bringing much more dissolution in a moment. However, local increased concentration prevent the later dissolution. As is shown in Figure 4.7 d), the smaller front of dissolved Ca$^{2+}$ is retarded in the decoupled model using tolerance of $10^{-3}$.

Figure 4.11, 4.12 show the coupling error and time step size for different tolerances during the simulation. It can be seen that the higher the tolerance, the larger the time step size. The profile of coupling error of the tolerance $10^{-3}$ fluctuates wildly because the time step size is increased too much. On the contrary, the lower tolerance results in smaller time step sizes and tiny fluctuations of the coupling error. From this observation, it can be assumed that tolerance will determine the stability of the solution.

The CPU time is plotted for the decoupled model using different tolerances in Figure 4.13. It can be seen that the chosen tolerance can strongly impact the efficiency.

As the tolerance is too low, the advantage of the decoupled model is not evident. As is shown in Table 4.7, the CPU time is 9574s for the decoupled model using tolerance of $10^{-5}$ with the average time step 2980 seconds while the CPU time is 9570s for the fully coupled model with maximum time step size 2080 seconds. But for the tolerance of $10^{-4}$ for the decoupled model the CPU time is only 895s. Additionally, the result of the tolerance of $10^{-4}$ is in good agreement with the fully coupled model.

Therefore, considering the efficiency and accuracy, tolerance $10^{-4}$ is to be applied in the decoupled model for the comparison of increasing grid resolution.
Figure 4.11: a)-b) Coupling error for the decoupled model using different tolerances. a) Coupling error for tolerances of \(10^{-3}\) and \(5 \cdot 10^{-4}\), b) Coupling error for tolerances of \(10^{-4}\), \(8 \cdot 10^{-5}\), \(5 \cdot 10^{-5}\), \(10^{-5}\).

Table 4.7: CPU time of the fully coupled model and the decoupled model using different tolerance

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<th>the decoupled model</th>
<th>CPU time (second)</th>
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<td>with tolerance of (10^{-3})</td>
<td>9574</td>
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<tr>
<td>maximum time step size 5080s</td>
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<td>3541</td>
<td>with tolerance of (10^{-4})</td>
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</tr>
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Figure 4.12: a)-b) Time step size for the decoupled model using different tolerances.

a) Tolerances for $10^{-3}$ and $5 \cdot 10^{-4}$, b) Tolerances for $10^{-4}$, $8 \cdot 10^{-5}$, $5 \cdot 10^{-5}$, $10^{-5}$. 

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4.4 Comparison of the accuracy and performance with increasing grid resolution between the decoupled and fully coupled model

In this section, different grid refinements are compared for the simulation of the base problem. The aim is to evaluate the accuracy and efficiency of the decoupled and fully coupled model with increasing unknowns.

Grid resolution used for the comparison for both models are illustrated in Table 4.8 and 4.9.

4.4.1 Results and discussion

Figure 4.14, 4.15, 4.16 and 4.17 compare the behavior of both models with regard to different element sizes.

For the coarse as well as for the fine grid, it can be observed that the front approximation of the coupled model does not significantly differ from the profile of decoupled model. As is expected, numerical diffusion is decreased if the grid is refined. Besides the front, near the injection point the approximations of fully coupled and the decoupled models have a similar trend. The pH is lowest for the finer and highest for the coarser grids. This is because the volume of the cell at the injection point in the finer grid is smaller than others. The advection time $\tau_A = \frac{\Delta x}{v}$ and with it the Damköhler number $D$
Figure 4.14: a)-b) Result of grid comparison for $C_{tot}$ for the decoupled and the coupled models. a) decoupled model, b) coupled model.
Figure 4.15: a)-b) Result of the grid comparison for Ca$^{2+}$ for the decoupled and the coupled models. a) decoupled model, b) coupled model.
Figure 4.16: a)-b) Result of the grid comparison for pH for the decoupled and the coupled models. a) decoupled model, b) coupled model.
Figure 4.17: a)-b) Result of grid comparison for $\Omega$ for the decoupled and the coupled models. a) decoupled model, b) coupled model.
Table 4.8: CPU time of the decoupled models with increasing refinement for the tolerance of $10^{-4}$.

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<th>Grid</th>
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<th>$\Delta y$</th>
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<th>cells in the y direction</th>
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<th>CPU Time(s)</th>
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</thead>
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<td>50</td>
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<td>50</td>
<td>302</td>
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<tr>
<td>2</td>
<td>1m</td>
<td>2m</td>
<td>100</td>
<td>1</td>
<td>100</td>
<td>895</td>
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<td>1m</td>
<td>100</td>
<td>2</td>
<td>200</td>
<td>1433</td>
</tr>
<tr>
<td>4</td>
<td>1m</td>
<td>0.5m</td>
<td>100</td>
<td>4</td>
<td>400</td>
<td>2623</td>
</tr>
<tr>
<td>5</td>
<td>0.5m</td>
<td>2m</td>
<td>200</td>
<td>1</td>
<td>200</td>
<td>3430</td>
</tr>
<tr>
<td>6</td>
<td>0.5m</td>
<td>0.5m</td>
<td>200</td>
<td>4</td>
<td>800</td>
<td>13492</td>
</tr>
</tbody>
</table>

Table 4.9: CPU time of the coupled model with increasing refinement, using a maximum time step size of 5080 seconds.

<table>
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<tr>
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<th>$\Delta y$</th>
<th>cells in the x direction</th>
<th>cells in the y direction</th>
<th>number of elements</th>
<th>CPU Time(s)</th>
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<td>1</td>
<td>50</td>
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<td>1</td>
<td>100</td>
<td>3215.7</td>
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<tr>
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<td>2</td>
<td>400</td>
<td>34565</td>
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<td>4</td>
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<td>0.67m</td>
<td>300</td>
<td>3</td>
<td>900</td>
<td>50075</td>
</tr>
</tbody>
</table>

Eq (2.29), is smaller for the finer grid [17]. The system is thus further away from a state of equilibrium for smaller cell volumes.

Next, in order to appraise the efficiency of both models for increasing unknowns, the execution time is compared. According to Table 4.8, 4.9, the corresponding CPU time is plotted with the number of the elements of each model in Figure 4.18. Wide differences of CPU time exists for the increased refinement for the two models. With increasing spatial elements, the decoupled model requires much less time than the coupled model for the test case.

The distribution of the coupling error for different grid discretization is shown in Figure 4.21. The level of coupling error for different grid discretization is around the tolerance $10^{-4}$. It was demonstrated that the coupled error is not only dependent on the tolerance, but also dependent on the spatial discretization. For coarser grids the coupling error has a highest peak while for finer grids discretization only fluctuating in a small range. As can be seen in Figure 4.22, when the cell number increases with grid refinement, decoupled model requires small time steps to reach convergence and coupling error is also limited sequentially. Figure 4.19 shows the decoupled model with the increasing refinement resolution can gradually converge to the coupled model with spatial discretization (grid
Figure 4.18: Comparison of CPU time for the decoupled and the coupled model for increasing number of elements.

100 1) at the injection point.

In addition, the increasing refinement of spatial discretization for the decoupled model decreased the smearing front in Figure 4.20. The front for the decoupled model using tolerance $10^{-4}$ with spatial discretization (grid 200 4) is sharper than the coupled model with spatial discretization (grid 100 1). However, the cost of CPU time for the decoupled model (grid 200 4) is 13492 seconds while the CPU time is 9570 seconds for the fully coupled reference model with spatial discretization (grid 100 1). From this point, the decoupled model with refined discretization has not much profit.

In the following it is investigated the effect of the refinement discretization on the y direction imposed on the accuracy and the efficiency. Figure 4.22 shows that the time step size is dependent on the grid refinement in the x direction. In other words, the refinement in the y direction can not decrease the coupling error. Figure 4.23 a)-c) also show the result of (grid 200 4) has a good agreement with the profile of (grid 200 1) and the finer grid in y direction can not reduce the numerical diffusion. However, concerning the efficiency, the CPU time for (grid 200 4) is 13492s while the CPU time is only 3430s for (grid 200 1).

However, it is compared the refined decoupled model (grid 200 1) using the tolerance $10^{-4}$ to the decoupled model with tolerance $10^{-4}$, $10^{-5}$ with grid discretization (grid 100 1) and the same spatial discretization of the fully coupled model in Figure 4.24. The front of decoupled model (grid 100 1) using tolerance $10^{-4}$ goes further than other models,
Figure 4.19: a)-b) Comparison of pH close to the injection. a) decoupled model, b) coupled model.
Figure 4.20: Front of mass fraction of Ca\textsuperscript{2+} for the decoupled models with different grid discretization and the coupled reference model (grid 100 1).

Figure 4.21: Development of coupling error in different grid resolutions using tolerance $10^{-4}$ for the decoupled models.
while the front of decoupled model using tolerance $10^{-5}$ is more steeper. Lowering the tolerance for the decoupled model could improve the result but the cost is large. As is shown in Table 4.10, CPU time for tolerance of $10^{-5}$ is around 11 times larger than tolerance of $10^{-4}$. However, the results of refined decoupled model (grid 200 1) has the sharpest front but CPU time is only 3 times larger than coarse grid decoupled model (grid 100 1) with the same tolerance.
Table 4.10: CPU time for different models.

<table>
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<th>model</th>
<th>CPU Time (second)</th>
</tr>
</thead>
<tbody>
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<td>3430</td>
</tr>
<tr>
<td>the decoupled model with the tolerance 10^{-4} and grid discretization(200 4)</td>
<td>13492</td>
</tr>
<tr>
<td>the decoupled model with the tolerance 10^{-5} and grid discretization(100 1)</td>
<td>9574</td>
</tr>
<tr>
<td>the decoupled model with the tolerance 10^{-4} and grid discretization(100 1)</td>
<td>895</td>
</tr>
<tr>
<td>fully coupled model with a maximum time step size of 2080s and grid discretization(100 1)</td>
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</tr>
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</table>

Table 4.11: Time steps over the different spatial discretization for the decoupled models.

<table>
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<th>nodes</th>
<th>number of steps</th>
<th>CPU Time (second)</th>
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Figure 4.23: a)-c) Comparison of grid (200 1) to grid (200 4) using the tolerance of $10^{-4}$ for the decoupled model. a) $C_{tot}$, b) pH, c) $Ca^{2+}$. 
Figure 4.24: a)-d) Comparison of the refined decoupled model (grid 200 1) using the tolerance $10^{-4}$ to the decoupled model with tolerance $10^{-4}$, $10^{-5}$ with grid discretization (grid 100 1) and the same spatial discretization of fully coupled model with a maximum time step size of 2080s. a) $C_{\text{tot}}$, b) pH, c) $\Omega$, d) $\text{Ca}^{2+}$. 

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5 Conclusion

In this thesis, the fully coupled model and the decoupled model are compared for one base problem.

An adaptive time step control based on the coupling error estimator is applied in the decoupled model. Different fixed tolerances of the decoupled models are compared to the fully coupled model. The main differences between the decoupled models and fully coupled model are around the front and close to the injection point where the highest reaction rate is observed. For the base problem, a tolerance of $10^{-3}$ is too high to control the coupling error and thereby causes oscillation. The profile of the decoupled model using tolerance of $10^{-5}$ has the best agreement with the fully coupled model. However, the tolerance influences the efficiency of the decoupled model considerably. The CPU time for the decoupled model using a tolerance of $10^{-5}$ is even larger than the CPU time for the fully coupled model. However, CPU time of the decoupled model with tolerance of $10^{-4}$ is only 9% of the fully coupled model for the same grid size. In addition, the result of the tolerance $10^{-4}$ is in good agreement with the fully coupled model. Therefore, $10^{-4}$ is chosen as the tolerance for the test case to control the time step size for the implemented decoupled model to ensure the model is both accurate and efficient.

The main contribution in this thesis is to investigate performance and accuracy of the implemented decoupled model in comparison to the fully coupled model with increasing grid resolutions.

It is shown that the decoupled model requires much less time than the coupled model for increasing refinement. Consequently, it is expected that the decoupled model could be a practical choice to simulate multi-component reactive transport processes for the large simulation domains.

Besides, it is demonstrated that there are two ways to improve the accuracy of the solution for the implemented decoupled model.

1) decreasing the tolerance for the time size control
2) refined grid resolution

To compare the accuracy of the solution of the decoupled model, the refined decoupled
model (grid 200 1) using the tolerance $10^{-4}$ is compared to the decoupled model (grid 100 1) with $10^{-5}$ and the fully coupled reference model (grid 100 1). Generally, all models are in good agreement with each other. However, the decoupled model (grid 200 1) with the tolerance $10^{-4}$ has the sharpest front. Furthermore, the cost of CPU time for the refined decoupled model is only 35% of CPU time for the decoupled model using the tolerance of $10^{-5}$. Therefore, the conclusion can be drawn that grid refinement for the decoupled model is a better way than to decreasing the tolerance of the coupling error for the decoupled model to acquire an accurate result for the test case.
Bibliography


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<td>Fractional flow formulation for two-phase flow in porous media</td>
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