IN-DEPTH WATER DIVERSION STRATEGIES

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Chapter 1

Abstract

In-depth water diversion is a chemical EOR method that has been winning acceptance over the last years because of several reasons. One of them is the fact that sodium silicate, active component, is considered a green chemical. Moreover, this component has shown the ability to generate thermally activated plugs at far away distances from the wellbore improving oil recovery. This work aims to give further understanding of how to approach the simulation of silica gelation kinetics, by integrating experimental data to a novel simulation approach for this process and how it can be applied to industry needs.

The simulations are performed using a thermal-compositional reactive formulation in Stanford’s Automatic Differentiation General Purpose Research Simulator (ADG-PRS) based on a fully implicit approach. The motivations for selecting this method is the strong coupling between chemical and flow variables linked to drastic changes in permeability profile and the absence of methods in literature addressing this subject consistently. The implementation of the silicates reaction assumes an oligomerization reaction through a fourth-order reaction rate describing the deposition of solid silicate along the reservoir. The methodology followed in this document is structured in three chapters: calibration and study of kinetics, comparison with a previous study and field applications.

Validation of the model displays a match between core experiments and simulations. Results from this section suggest a strong dependence on upscaling of the reaction rate constant and encourage further research on this topic. Study of kinetics, from a simulation perspective, reveals that the process time scales and local domain play a major role in resolution. Numerical convergence of the solution was achieved for a two-meter grid along the flow direction and simulation timesteps below 1 day. Results from comparison with previous works show great differences in the formation of the in-depth silicate plug. The prescription of the equation as a solids deposition proposes more realistic results in terms of plug distribution and activation. Moreover,
cumulative oil production improvements rounding 7% over a fields file, account for realistic figures. The application on channeled subsurface confirms the possibility of implementing the process on more realistic subsurface. A clear optimization of the water sweep around the plugged zones is evidently leading to improvements, rounding the percentage mentioned above. Contrary to expectations, after introducing a blockage, no major variation in flow towards producer’s perpendicular to the main channel are observed. In the geothermal applications, the generation of a plug helps to increase the thermal breakthrough time, extending the geothermal doublet lifetime.

The overall process has proved to be sensitive to parameters such as silicate concentration in solution, the volume of a pre-flush batch and the volumes of silicate solution injected. These factors give room for optimization of the process for future studies.
Chapter 2

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Chapter 3

Introduction

The many years of exploration and production in the industry have left the shallow and relatively easy reservoirs drained. Nowadays, the industry is challenged by having to work with deeper and less conventional reservoirs. This scenario has encouraged scientists and engineers to innovate through applications such as Enhanced Oil Recovery (EOR) methods. Although some of these EOR methods are widely used (e.g. gas and polymer injection), others like in-depth water diversion are still being developed.

For its chemical nature, in-depth water diversion is classified as a chemical EOR method. It is based on the injection of materials designed to travel along the reservoir and activate when meeting certain conditions (e.g. chemical or thermal). The most common application currently targets the improvement of oil recovery within reservoir containing highly permeable paths. In these cases, sodium silicate is injected into the reservoir where it travels until reacting and forming gels. In this state, sodium silicate withstands large pressure gradients becoming an effective plug with the potential of generating permeability profiles changes and therefore diverting water to unswept zones of the reservoir.

In the past, few alternatives were available for in-depth methods and most applications aimed for the near wellbore zones. However, recent studies showed the potential of sodium silicate to generate effective plugs [15] and by being classified as green chemical in the PLONOR list [4], these chemical has revived research in this field.

From this point forward, in-depth water processes have been reported mainly in the North Sea with pilot wells in the Gullfaks field [29, 30] and extensively later in the Snorre field by [28, 13, 14, 15]. Along with field implementation, some experimental work has been documented, gathering information from the chemical reactions, activation mechanisms and behavior at core scale [9, 1, 28, 29, 23, 11]. On the other hand, fewer efforts have been documented on simulation of this process leading to few studies, mainly reported by [14, 23, 1]. When compared to field and experimental
work, a clear gap is evident for simulation of this process.

Simulation has proved to be a key factor while developing technologies. It allows an accelerated understanding of physical phenomena while elucidating alternatives or announcing problems otherwise expensive if discovered during operations. For these reasons, we believe that investing in simulation research can bring valuable insight of the process. Literature referring to this topic reveals research opportunities in methodology, physics prescription and identification of the control parameters. In the first, only loosely coupled or uncoupled simulation techniques have been tested. For the second, incorporation of interdependent variables is needed. For the latter, identification and quantification of control parameters are essential. Acknowledging these opportunities, research in this study aims to answer the question which method has to be implemented and which parameters have to be identified in order to generate an accurate simulation of an in-depth water diversion process?

Seeking an answer to the question above, the following hypothesis will be tested in this study. An implementation of a fully implicit method is required to solve the coupled physics of the process. A simple chemical reaction can be prescribed to represent the gelation of sodium silicate. The reaction kinetics will lead to different numerical resolution as those proposed for transport problem. The simulation method will allow enough confidence to identify and quantify the process control mechanisms. These hypothesis capture and guide the scope of this work.

The carry on this task, the following methodology is implemented. A fully implicit approximation will be used to solve the expected coupled physics of this chemical-transport problem. The simulation approach follows the research line implemented at Stanford University in the Automatic Differentiation General Purpose Research Simulator (ADGPRS) by Farshidi [26]. At the Technical University of Delft, this implementation was extended by Fuciño’s in his M.Sc work [? ] where he introduced a model accounting for changes in porosity-permeability due to in-situ kerogen upgrading. The contribution to the methodology proposed in this thesis refers to the adaptation and validation of the porosity-permeability model by Fuciño to incorporate reactions that reduce the porous space. The results from this method will be compared to different approximations documented in literature.

For the study of kinetics, the methodology approaches resolution via a sensitivity study of time and space parameters, with the aim to clarify if extended precision is needed when compared to regular transport problems. Moreover, effects of upscaling, regarding the reaction rate parameter, will be qualitatively addressed through detailed comparison of core and reservoir scale simulation results.

In the chemical domain, the 4-species reaction modeling is challenged by a 5-species
reaction proposition. This reaction although not new, proposed by Icopini in 2004, has not been used in the simulation. Comparison of the two is expected to give insight into the chemical representation of the process.

Finally, the methodology to identify and quantify the effect of the control parameters will be performed through a sensitivity study targeting two objectives. First, effects on permeability profiles due to perturbations in inputs. Second, effects on oil recovery due to the same perturbations.
Chapter 4

State of the art

This chapter summarizes the in-depth water diversion process along with the work performed in the oil industry. Moreover, description of the physical concept is presented and the mathematical models are detailed.

4.1 In-depth water diversion in the oil industry

In-depth water diversion refers to the process of generating severe permeability profiles reduction within a reservoir at distances far away from the injection well. Because of its chemical nature, this process is classified as a chemical Enhanced Oil Recovery (EOR) technique in the oil industry literature. The most relevant difference with other permeability reducing processes is the distance at which the profiles are modified. Most techniques, such as polymer or well injection, act on the near wellbore area and focus either on water-shutoff treatments or fracture control. Instead, in-depth water diversion, as its names suggest, has for purpose the deviation of water to poorly swept reservoir zones with the goal of improving the oil recovery. A good schematic representation of the process is depicted by Skrettingland in [14], see Fig B.1.
In-depth methods are dated to a relatively recent discussion in the literature around 1990’s. Before it, mainly near well diversion was discussed. However, since the sodium silicate is considered a green chemical, the processed potential expanded. The chemistry of silica gelation dates back to the 70’s with extensive literature studies mainly in [24] and later by other authors [3, 19, 9]. Nevertheless, an active use in well pilots is reported only after the 90’s, mainly in the Gullfaks field at the North Sea [29, 30] and extensively later in the same region in the Snorre field by [28, 13, 14, 15].

For in-depth water diversion purposes, sodium silicate is one of the few chemicals to be extensively studied because of its classification as a green chemical. Most of the experimental work, performed in this matter, includes the description of the gelation times, the rate of reaction, retardant agents and core experiments. Relevant literature on this topic is detailed by [9, 1, 28, 29, 23, 11]. From the experiments, it is crucial to highlight the reaction rate estimation reported by Icopini and Hiorth. Even though their experiments were carried for bulk sodium silicate at ambient temperature, the results are essential for model calibration. Moreover, experiments on cores from Berea and Bentheimer sandstone, from Stavland and Jurinak, give an understanding of the permeability profile reduction.
Several efforts by different authors have reported the evolution of computer simulation of this technique [14, 23, 1]. In [14], Skrettingland et al. models the permeability reduction from sodium silicate injection by matching concentration and temperature pre-established criteria. This simulation approach, even though not governed by an accurate differential equations, was implemented based on a conventional reservoir simulator, Eclipse 100, which doesn’t include a chemical module.

A more detailed study by Huseynov in [23] includes the adsorption term to the mass balance equation to represent the in-depth process. The simulator for this purpose was REVEAL from Petroleum Experts which includes thermal and water chemical modules. A disadvantage of this implementation is an employment of the IMPES (Implicit Pressure Explicit Saturation) scheme which significantly restricts the performance of a coupled reactive flow and transport processes.

Furthermore, in [1], Hiorth et al. suggest a third alternative to model water diversion by sodium silicate deposition. Similar to the previous models, this method includes a source term in the transport equation describing in-depth divergence. The main disadvantage in this work is the need of combining two simulators, one for the chemical reaction and one for transport. This approach is considered loosely coupled and could lead to misguiding results when modeling a strongly coupled phenomena.

Overall, the simulation methods described, use either loosely coupled or uncoupled techniques for the chemical-transport phenomena. In principle, most chemical reactions are not expected to alter the flow and therefore can be modeled as described by the authors above [8]. However, the chemical reaction for in-depth water diversion generates a severe permeability reduction that drastically changes the flow. As consequence, it is expected to have a strongly coupled physics for this process. Moreover, no discussion was found in the literature regarding compositional simulation to trace species, resolution and convergence of chemical-transport, reaction kinetics and parameters sensitivity. For this reason, large improvements should be performed in simulation technique of this process.

The above-mentioned laboratory and simulation efforts have been combined in several field pilots. Major activity, regarding this process, has been carried forward in the North Sea, where pilot wells are reported in the Gullfaks and Snorre fields [30]. For the first case, the authors report an expected increase in production of 130,000 Sm$^3$ over five years and an effective reduction in water cut by 13%. Additionally, it was estimated that the treatment penetration was 20 meters from the injector creating a residual resistivity factor ($RRF = k_o/k_f$) between 30 and 50 $[mD/mD]$. However, the expected recovered volumes proved to be less than a half of the expected based on simulations prior to the silicate injection. In the Snorre case [15], authors report in-depth plug generated at approximately 40 meters with an $RRF$ of more than 100
To the moment, no production data is reported from this case.

A large amount of work has been put together to detail and understand in-depth water diversion through the sodium silicate injection. Although few data has been recovered from field pilots, there is still substantial room for improvement in the experimental and simulation fields.

4.2 Chemistry of silica gelation

Sodium silicate has regained popularity in the oil industry for being considered a green chemical (PLONOR) and for its potential in in-depth water diversion applications. Originally, this chemical was mostly used for near well treatments, however, after used in operations in the Gullfaks and Snorre field for in-depth treatments, its reputation has increased significantly.

Silica has been extensively studied in [24], where Iler devotes a full chapter to the gelation process. He reports three stages for polymerization which comprise the particle growth from monomers to branded chains. A good visualization of the Silica’s polymerization process is presented in Fig. 4.2.

![Illustration of Silica polymerization by [24]](image)

There is a general agreement to consider the condensation of silanol groups (aqueous silica solution) as starting point of the polymerization process. The chemical reaction

\[ mD/mD \]
to this process is given by:

$$H_4SiO_4(aq) + H_4SiO_4(aq) \xrightarrow{k} H_6Si_2O_7(aq) + H_2O \quad (4.1)$$

In this equation, the terms to the left represent the silica monomers while the first term to the right the silica dimer. Other authors like Icopini report a further step of the polymerization reaction. His studies show that reactions (4.1) reach equilibrium very fast, while the growth from monomers to tetramers (4 monomer structure), presented below, introduces a more detail description of the overall polymerization rate.

$$H_8Si_3O_{10}(aq) + H_4SiO_4(aq) \rightarrow H_8Si_4O_{12}(aq) + 2H_2O \quad (4.2)$$

Assuming any of these two equations as a description of the polymerization process, the equation describing the overall loss of monomeric silica in solution is presented by [9] as an order four reaction rate of the concentration:

$$\frac{d[H_4SiO_4(aq)]}{dt} = -k[H_4SiO_4(aq)]^4 \quad (4.3)$$

In this equation, the concentration represented by square brackets has molar units, and the reaction rate, denoted by $k$, is in [molar/s] units.

Several authors [24, 9] agree on describing the driving mechanisms of the process as being the pH, temperature, salinity and concentration. Some of these parameters, like temperature and salinity, are accounted in the rate of reaction. More complex one, for example, pH, require a further study of their own. From a broad perspective, at low pH, particles growth is almost negligible whilst at pH greater than 7, growth continues to larger particle sizes [24]. A complete mathematical description of these mechanisms is included in the reaction term presented by [1]. The description accounts for temperature, salinity, concentration and buffer solution (HCl):

$$k^{-1} = a\xi e^{\beta[HCl]} e^{\gamma\sqrt{|Ca|}} e^{-\frac{E_a}{RT}}. \quad (4.4)$$

In this equation, [HCl] stand for the concentration of chlorhydric acid in solution in weight percentage (w%), [Ca] for the concentration of Calcium in ppm and $e^{-\frac{E_a}{RT}}$ is the arrhenius equation accounting for temperature with activation energy $E_a$ in $kJ/mol$, R in $kJ/mol \cdot K$ and T in $K$. The terms $a$, $\xi$, $\beta$ and $\gamma$ are all parameters fitted from experiments and have the following units respectively: dimensionless, [days], [1/w%] and [1/\sqrt{ppm}].
4.3 Reservoir simulation

Numerical solution of Partial Difference Equations (PDE’s) has been a topic of extensive study in the literature. The most widely used include Finite Difference Method (FDM), Finite Volume Method (FVM) and Finite Elements Method (FEM). Among these, the FVM has won popularity for solving PDE’s related to flow and transport due to the conservation of the method [21]. FVM was first introduced to the field of fluid mechanics in 1970s [18] and is used widely ever since.

The structure of this method rests on the application of the Divergence Theorem to the PDE in conservative form. This allows the approximation of the integrals of the flux as linear integrals over the control volume. These last ones can then be approximated by a finite difference discretization in several ways. Some of them are a one-sided approximation, centered approximation and higher order approximation. Each of these methods inherits an approximation error called the truncation error caused by truncating the Taylor series expansion of the function. The truncation errors are $O(h)$, $O(h^2)$ and higher order accordingly [18].

Discretization in time is generally divided into explicit (Euler forward method), implicit (Euler backward method), and higher-order methods. The selection between implicit and explicit lies mainly in two criteria - computer cost and stability. While the partially explicit form incurs in less computational cost due to a smaller Jacobian, result’s convergence is restricted to the time and space discretization by a relationship known as CFL number [21]. On the other hand, the implicit method requires a larger Jacobian computation resulting in a stable solution regardless of the CFL. Explicit models have proven to be very useful when solving decoupled problems. Nevertheless, it is because of stability of the solution that most simulation codes are built on an implicit model basis.

Selecting the right approach is a fundamental part of the solution when using numerical methods. However, the most important part is the numerical convergence of the solution. Knowing that the solution of a numerical method is an approximation of the real solution, the concept of convergence is essential to determine how good is the approximation.

The concept of convergence includes two sub-concepts: consistency and stability. The first is related to the order of the error, while the latter refers to the error over time. Consistency discusses how well the approximation reproduces the real solution, also known as local truncation error. This error is directly dependent to the method used in the discretization on the PDE’s and is usually denoted as $O(h^p)$, where h is the mesh size and p the order of the error. A method is said to be consistent if the truncation error is of order $O(h^p)$ where $p \geq 1$, in which case the consistency is of
order p. Stability implies that the error doesn’t grow over time, in other words, the error must be bounded. If the error at some point in time is the accumulated error plus the local error at that time step, [21] shows that it can be expressed as:

$$E_k(t_n) = H_k^n(o) - k \sum_{i=1}^N H_k^{n-i} L_k(t_{i-1})$$

(4.5)

And through Lax-Richtmyer stability, he defines that a method is stable if for each time steps there is a constant Cs and a value Ko such that

$$\| H_k^n \| < C_s$$

for all nk < k, C_o

(4.6)

Generally, the method is stable if $H_k$ is less than 1.

Section 4.1 briefly discussed the simulations methods and simulators implemented in previous studies. In general, it was found that most commercial simulators still lack multi physics modules that can handle chemical transport phenomena. Additionally, the solution strategies proposed by these software are a combination of Implicit-Explicit methods which are loosely coupled. Therefore, commercial alternatives do not seem appropriate to address these physical phenomena.

The simulator destined for this study is the Stanford University’s Automatic Differentiation General Purpose Research Simulator (ADGPRS). The advantages of ADGPRS compared to other simulators are the availability of a chemical module that can handle kinetic and equilibrium reactions, the option for choosing both natural an overall compositional variable formulations, and fully implicit solution method [6]. In the past, this simulator has extensively been used to address research studies with both fully implicit formulations and chemical transport phenomena [26, 22, 7].

### 4.4 Compositional transport

Fluid flow has been widely studied by fluid mechanics through Navier-Stokes and mass balance equations. However, when porous media applications are addressed, Darcy’s equation is used instead of Navier-Stokes.

$$\vec{u}_p = \frac{-K k_{rp}}{\mu_p} \left(\nabla P - \rho_p g \nabla D\right)$$

(4.7)

In this equation $u_p$ is Darcy’s velocity, $K$ is the permeability tensor, $k_{rp}$ is the phase relative permeability, $\mu_p$ the phase viscosity, $P$ the pressure, $\rho_p$ the phase density, $g$ the gravity and $D$ the depth.

Assuming the conservation of a property over a control volume, in this case mass, the flow in time is related to the flow through the boundaries plus any source in the
control volume.

\[ \text{accumulation} + \text{flux} = \text{source} \quad (4.8) \]

\[ \frac{\partial}{\partial t} \left( \sum_{j=1}^{n_p} (\phi \rho S_j) \right) + \nabla \cdot \left( \sum_{j=1}^{n_p} (\rho_j \vec{u}_j) \right) = q_I \quad (4.9) \]

Incurring in several assumptions such as no gravity, no source term, incompressible, two-phase and 1D flow, the mass balance equation reduces to:

\[ \phi \frac{\partial S_w}{\partial t} - \lambda_w \frac{\partial^2 p}{\partial x^2} = 0 \quad (4.10) \]

This is the general equation applied for Oil-Water application and because of the assumptions above, this problem is rather simple and can be solved through the method of characteristics introducing a fractional flow formulation. The equation 4.10 reduces to

\[ \phi \frac{\partial S_w}{\partial t} + u_w \frac{\partial f_w}{\partial x} = 0 \quad (4.11) \]

In this method, the solutions must comply with the two conditions. First, velocities of the moving front always increase monotonically to a maximum known as the shock velocity. Second, the solution must comply with the entropy condition which states that the velocity of the upstream saturation must be equal to the shock velocity [16].

In a compositional model, the phases of a system are described as a mix of the components within. In such a model, the properties of the phases vary proportionally to the components composition. In petroleum engineering, compositional models are mostly used to describe systems in which oil is partition in several hydrocarbons (C1, C2, ..., Cn), However, the application of this models also covers topics such as gas injection, gas condensate systems, chemical flooding and many EOR processes.

Since this kind of model gives a more insightful description of the system, it incurs in an important drawback regarding computational cost. In the mathematical description, each additional component increases by one the number of equations to be solved. Moreover, the complexity of phase behavior calculations is increased as phase stability and distribution of components per phase are necessary.

Returning to the mass balance equation with molar fractions, the conservation is presented per component over all the phases of the system in the following form:

\[ \frac{\partial}{\partial t} (\phi \rho_T Z_i) + \nabla \cdot \left( \sum_{j=i}^{N_p} (\rho_j X_{ij} \vec{u}) \right) = q_i^W \quad (4.12) \]
In this equation, \( \rho_T \) represents the total molar density, \( Z_i \) the molar fraction per component, \( \rho_j \) the phase molar density, \( X_{ij} \) the molar fraction per phase \( (x_j, y_j, w_j, \ldots, \text{etc.}) \).

Furthermore, phase stability and components distribution, which describe the phase state (solid, liquid or gas) and the distribution of component per phase, add two sets of nonlinear equations to the system.

Phase equilibrium assumption tells that fugacity is equal among the phases. Resulting in the following set of equations:

\[
f_{i1} = f_{i2} = \ldots = f_{ij} = f_{in_p}
\]
\[
i = 1, ..., n_c
\]
\[
j = 1, ..., n_p
\]

Where \( i \) represents the number of components, \( j \) the number of phases and \( f_{ij} \) the fugacity of component \( i \) in phase \( j \).

An alternative option to the phase stability calculations is the K-value method. In this approach, a relation of the components distribution per phase is known a priori. The relationship noted as K-value, is the ratio of the components per phases. This ratio assumes phase distribution at equilibrium for a given pressure, temperature and composition.

\[
k_i = \frac{y_i}{x_i}
\]

In this equation, \( y_i \) is the fraction of component \( i \) in gas phase and \( x_i \) the fraction of component \( i \) in liquid phase.

Referring to flash calculation, it represents the phases distribution of each component

\[
F(V) = \sum_{i+1}^{N} \frac{z_i(1 - K_i)}{V(K_i - 1) + 1} = 0 \tag{4.15}
\]

\[
y_i = \frac{z_iK_i}{V(K_i - 1) + 1}
\]

In order to solve this system, the following closing equations are needed:

Fraction of components per phase

\[
\sum_{i=1}^{n_c}(X_{ij} - 1) = 0 \tag{4.16}
\]

Fraction of phases

\[
\sum_{i=1}^{n_p}(v_j - 1) = 0 \tag{4.17}
\]
Overall molar fraction

\[
\sum_{i=1}^{n_c} (Z_{ij} - 1) = 0 \tag{4.18}
\]

Therefore, a system of \(n_c\) components and \(n_p\) phases will have \(1 + n_c + n_p \times n_c\) unknowns \((P, Z_{nc}, X_{nc \times np})\). Therefore, it will be described by \(n_c\) equations from mass transport, 1 equation from overall molar fraction, \(n_p \times (n_c - 1)\) from fugacities or K-vales, and \(n_p\) equations from fraction of components per phase.

### 4.5 Reactive transport

When referring to chemical transport, the first distinction is the type of reaction taking place. Generally, reactions can be divided into equilibrium and kinetic reactions. The first considers processes which are reversible and reach equilibrium almost instantaneously. The latter covers process occurring only in one direction and require a kinetic rate law to determine the reaction rate [8]. Since the gelation of silica is an irreversible process, only the description of kinetic reaction is discussed from this point forward.

In general terms, a kinetics reaction can be unimolecular, bimolecular or termolecular depending on the number of species, molecules, interacting [20]:

\[
a \xrightarrow{k} b + c
\]
\[
a + b \xrightarrow{k} c + d
\]
\[
a + b + m \xrightarrow{k} b + c + m
\]

Furthermore, accounting for the law of definite proportions, the species react in quantities defined as stoichiometric coefficients. For a bimolecular reaction, this means:

\[
Aa + Bb \xrightarrow{k} Cc + Dd \tag{4.20}
\]

where A, B, C and D correspond to the stoichiometric coefficient of each species. Moreover, the definite proportions law states that the changes of species over time is proportional to the stoichiometric coefficients in the following way:

\[
\frac{n_a(t) - n_a^0}{A} = \frac{n_b(t) - n_b^0}{B} = \ldots = \frac{n_N(t) - n_N^0}{N} = \xi(t) \tag{4.21}
\]

Here \(\xi(t)\) is the extend of reaction.

According to [20], the above equation for a given i-th species and differentiating over time can be arranged as follows:

\[
n_i(t) = n_i^0 + N\xi(t) \tag{4.22}
\]
\[ \frac{dn_i}{dt} = N \frac{d\xi}{dt} = Nk \] (4.23)

where \( k \) is the reaction rate. Discretizing over time gives:

\[ \delta n = N \delta \xi \] (4.24)

Accounting for all the reactions taking place in the system

\[ \delta n_i = \sum_{r=1}^{N_R} \delta n_i = \sum_{r=1}^{N_R} v_{ir} k_r \] (4.25)

In this equation \( v_{ir} \) represents the stoichiometric coefficients per component per reaction. Or back to a continuous time as:

\[ \frac{dn_i}{dt} = \sum_{r=1}^{N_R} v_{ir} k_r \] (4.26)

This term is the same as the source term in the mass transfer equation.

### 4.6 Energy Equation

When referring to the energy equation, there are usually terms considered: the internal, kinetic and potential energy. The sum of all parts gives the total energy balance for the system [16]:

\[ \text{Total Energy} = U_T = U_{\text{internal}} + U_{\text{kinetic}} + U_{\text{potential}} \] (4.27)

For porous media describing subsurface reservoirs, we usually account for changes in internal energy only. For the energy in the control volume, an additional distinction between the energy from the fluids and the energy from the rock is necessary. Written in terms of internal energy, the equation reads:

\[ U_T = U_{\text{fluid}} + U_{\text{rock}} = \phi \sum_j S_j \rho_j U_j + (1 - \phi) C_r (T - T_{\text{ref}}) \] (4.28)

In this equation, \( U_j \) is the internal energy of phase \( j \), \( C_r \) accounts for the rocks specific heat capacity and \( T \) for the temperature.

**Accumulation**

For a system with \( j \) phases, the accumulation term can be written in the following form:

\[ \frac{\partial}{\partial t} \left( \phi \sum_{j=1}^{N_p} S_j \rho_j U_j + (1 - \phi) C_r T \right) \] (4.29)
Energy flux
Generally, the energy transported has contributions from the convection and conduction terms. Here, the heat transfer by radiation or diffusion is neglected:

$$\nabla \cdot \left[ \sum_{j=1}^{N_p} \rho_j H_j \vec{u}_j - k_T \nabla T \right]$$

(4.30)

We introduce phase enthalpy which can be defined as:

$$H_j = U_j + v_j / \rho_j$$

(4.31)

Source
The source terms consider the inflow of heat with heat losses can be noted as:

$$q_h = \sum_{j=1}^{N_p} \left[ \rho_j H_j q_j + q_h \right]$$

(4.32)

The full energy equation per component can be expressed as noted below:

$$\frac{\partial}{\partial t} \left[ \phi \sum_{j=1}^{N_p} S_j \rho_j U_j + (1 - \phi) \rho_{rock} C_{rock} T \right] + \nabla \cdot \left[ \sum_{j=1}^{N_p} \rho_j H_j \vec{u}_j - k_T \nabla T \right] + \sum_{j=1}^{N_p} \rho_j H_j q_j + q_h = 0$$

(4.33)
Chapter 5

Methodology

This chapter describes the overall scheme followed to prove the hypothesis formulated in chapter 3. Herein, the numerical discretization and solution method are explained. The chemical reactions and permeability formulation are proposed and organized in 4 models. The model calibration is discussed in the study of kinetics. The chapter closes with explanation of how the model can be implemented in field applications.

5.1 Numerical Method

This section details the discretization and Newton’s method solution scheme implemented in the fully implicit formulation.

5.1.1 Overall Scheme

Chemical-compositional transport problems involve the solution of several PDE’s, along with some algebraic equations. Most of the physics involve high orders of non-linearity originated from the chemical and compositional domain.

The discretization schemes use in this work are central difference approximation with upstream weighting for space and backward Euler approximation in time [21]. To solve the corresponding nonlinear problems, the iterative Newton’s method will be followed (Fig. 5.1).
5.1.2 Compositional transport discretization

Mass transport phenomena are described by a hyperbolic equation usually denoted as the Cauchy problem [21]. Generally, these equations are not stiff like the parabolic (conductive heat) equation, a reason why there is a tendency to use explicit rather than implicit methods. Nevertheless, since several problems will be solved simultaneously, implicit methods are preferred to avoid stability difficulties while choosing an appropriate timestep.

The mass conservation transport problems can be approached by two different methods: the natural variable formulation and the molar variable [10, 5]. Depending on which methodology is used, the general iterative solution path in reactive formulation varies [26]. The latter formulation has been selected for this work because of its reduced number of unknown variables which translated to a simpler Jacobian construction [5]. Moreover, the compositional domain is simplified by means of a K-values formulation where each $k_{ij}$ value are defined a priori from equilibrium conditions.

The method follows the research line implemented in Automatic Differentiation General Purpose Research Simulator (ADGPRS) using overall composition formulation [5]. A mass transport system accounts for $n_c + 1$ variables ($P_1, Z_1, ..., Z_{n_c}$) which are solved by a set of $n_c$ differential transport equation plus 1 molar fraction equation of
the form:
\[
\sum_{i=1}^{n_c} Z_i = 1
\]  
(5.1)

In the natural variables formulation, the primary and secondary variables are solved simultaneously. By contrast, in the molar formulation, the secondary variables are assumed to be fully converged during each Newton iteration by applying a constraint to the primary solution [5].

Mass conservation over a control volume includes an accumulation term A, a flux term F, source term S and a reactive term R (the last terms term will be noted under the reaction discretization). Under this assumption, the mass conservation equation for a fluid is:
\[
A + F + S = 0
\]  
(5.2)

\[
\frac{d}{dt}(\phi p_T Z_i) + \nabla \cdot \sum_{j=1}^{n_p} (\rho_j x_{ij} \vec{u}_j) + \sum_{j=1}^{n_p} x_{ij} \rho_j q_j = 0
\]  
(5.3)

\[
V \left[ (\phi p_t Z_i)^{n+1} - (\phi p_t Z_i)^n \right] - \Delta t \sum_l \left( \sum_{j=1}^{N_p} x_{ij} \rho_j^l \Gamma_j^l \Delta \psi^l \right) + \Delta t \left( \sum_{j=1}^{n_p} x_{ij} \rho_j q_j \right) = 0
\]  
(5.4)

In the previous equation, we use a two-point flow approximation with upstream weighting where \(\Gamma^l\) is a pressure potential over an interface \(l\) and \(\Gamma^l\) correspond to the transmissibility [17]. Note that the approximation for transmissibility is separated into two parts. The first, geometric term, treats absolute permeability and block properties. The second term includes fluid properties. The approximation for the geometric part is performed by harmonic average. The fluid properties term is approximated using upstream weighting [12].

The residual function of the equation above is, therefore, a function of the following variables.

\[ R^{t+1} = f(P^{t+1}, Z^{t+1}, X^{t+1}, T^{t+1}, \phi^{t+1}) = 0 \]  
(5.5)

Linearizing the residual:

\[ R^{t+1} \approx R^{v+1} \approx R^v + \frac{\partial R^v}{\partial P} \delta P^{v+1} + \frac{\partial R^v}{\partial Z} \delta Z^{v+1} + \frac{\partial R^v}{\partial X} \delta X^{v+1} + \frac{\partial R^v}{\partial T} \delta T^{v+1} + \frac{\partial R^v}{\partial \phi} \delta \phi^{v+1} = 0 \]  
(5.6)

Finally, compositional transport in matrix form for \(n_c\) components takes the form
5.1.3 Chemical transport discretization

Reactions can take place in both fluid species and solid species. In this study, it is assumed that solid species are not transported and therefore are deposited in the matrix and changing porosity. Therefore, the reactive transport mass conservation for liquids and solids components are:

\[ A + F + S + R = 0 \] (5.7)

**Liquids**

\[
\frac{d}{dt} (\phi \rho_T Z_i) + \nabla \cdot \left( \sum_{j=1}^{n_p} (\rho_j X_i \bar{u}_j) + \sum_{j=1}^{n_p} x_{ij} \rho_j q_j \right) + \sum_{k=1}^{n_k} v_{ik} r_k + \sum_{q=1}^{n_q} v_{iq} r_q = 0
\] (5.8)

**Solids**

\[
\frac{d}{dt} C_m = \sum_{k=1}^{n_k} v_{ik} r_k + \sum_{q=1}^{n_q} v_{iq} r_q
\] (5.9)

Where k represents the kinetic reactions and q the equilibrium reactions. Neglecting all the equilibrium reactions and imposing the same assumptions of compositional transport, the equations can be discretized as follows:

**Liquids**

\[
V \left[ (\phi \rho_T Z_i)^{n+1} - (\phi \rho_T Z_i)^{n} \right] - \Delta t \sum_{l} \left( \sum_{j=1}^{N_p} x_{ij} \rho_j \Gamma_j^l \Delta v_j^l \right) + \Delta t \left( \sum_{j=1}^{n_p} x_{ij} \rho_j q_j \right) + \Delta t \left( \sum_{k=1}^{n_k} v_{ik} r_k \right) = 0
\] (5.10)

**Solids**

\[
V \left[ (C_m)^{n+1} - (C_m)^{n} \right] + \Delta t \left( \sum_{k=1}^{n_k} v_{ik} r_k \right) = 0
\] (5.11)
The residual for this equation can, therefore, be constructed from the transport and the reaction terms and is a function of the following variables:

\[ R_{t}^{t+1} = R_{flow}^{t+1} + R_{reaction}^{t+1} \]  

(5.12)

\[ R_{total}^{t+1} = f(P^{t+1}, Z^{t+1}, X^{t+1}, T^{t+1}, \phi^{t+1}, C^{t+1}) = 0 \]  

(5.13)

Linearizing the residual

\[ R_{v}^{v} + \frac{\partial R_{v}^{v}}{\partial P} \delta P^{v+1} + \frac{\partial R_{v}^{v}}{\partial Z} \delta Z^{v+1} + \frac{\partial R_{v}^{v}}{\partial X} \delta X^{v+1} + \frac{\partial R_{v}^{v}}{\partial T} \delta T^{v+1} + \frac{\partial R_{v}^{v}}{\partial \phi} \delta \phi^{v+1} + \frac{\partial R_{v}^{v}}{\partial C} \delta C^{v+1} = 0 \]  

(5.14)

Finally, compositional transport in matrix for \( n_c \) components is expressed as

\[
\begin{bmatrix}
\frac{\partial R_{v}^{v}}{\partial P} & \frac{\partial R_{v}^{v}}{\partial Z} & \frac{\partial R_{v}^{v}}{\partial X} & \frac{\partial R_{v}^{v}}{\partial T} & \frac{\partial R_{v}^{v}}{\partial \phi} & \frac{\partial R_{v}^{v}}{\partial C} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\frac{\partial R_{nc}^{v}}{\partial P} & \frac{\partial R_{nc}^{v}}{\partial Z} & \frac{\partial R_{nc}^{v}}{\partial X} & \frac{\partial R_{nc}^{v}}{\partial T} & \frac{\partial R_{nc}^{v}}{\partial \phi} & \frac{\partial R_{nc}^{v}}{\partial C}
\end{bmatrix}
\begin{bmatrix}
\delta P^{v+1} \\
\delta Z^{v+1} \\
\delta X^{v+1} \\
\delta T^{v+1} \\
\delta \phi^{v+1} \\
\delta C^{v+1}
\end{bmatrix}
= \begin{bmatrix}
-R_{v}^{v} \\
-R_{nc}^{v}
\end{bmatrix}
\]

The contribution of this study lies in the modification of the porosity-permeability variations prescribed by Fuciño’s in \[22\]. This model is detailed further in section 5.2.

### 5.1.4 Thermal equation discretization

According to \[17\], the equation 5.15 can be discretized for an unstructured grid and a backward Euler approximation in time in the following way:

\[
V \left[ \left( \phi \sum_{j=1}^{N_p} S_j \rho_j U_j + (1 - \phi) U_r \right)^{n+1} - \left( \phi \sum_{j=1}^{N_p} S_j \rho_j U_j + (1 - \phi) U_r \right)^{n} \right] - \\
\Delta t \sum_{l} \left( \sum_{j=1}^{N_p} h_j \rho_j \Gamma_j \Delta \psi_l + \Gamma_c \Delta T_l \right) + \Delta t \left( \sum_{j=1}^{N_p} h_j \rho_j q_j + q_h \right) = 0
\]  

(5.15)

In the previous equation, we use a two-point flow approximation with upstream weighting where \( \Delta \psi_l \) is a pressure potential over an interface \( l \), \( \Delta T_l \) a difference in temperature over neighboring blocks and \( \Gamma_l \) correspond to the conductive transmissibility which includes thermal conduction of all phases and geometry \[17\].
5.1.5 Residual

If we consider the full set of unknowns in the system as a vector of the form
\[ \mathbf{X} = [P, Z_1, ..., Z_{nc}, C_1, ..., C_{nm}, X_1, ..., X_{np}, v_1, ..., v_{np}, \phi]^T \]  
(5.16)

This set can be divided into two subsets. One is called the primary and contains the pressure, molar fractions and the minerals concentrations. The secondary subset containing the compositional variables. In this way, the global mass balance equation is separated from the phase equilibrium ones which are local. This split aims to apply different solution methods for each set.

\[ \mathbf{X} = (X_p, X_s)^T \]
(5.17)

\[ X_p = [P, Z_1, ..., Z_{nc}, C_1, ..., C_{nm}, \phi]^T \]
\[ X_s = [X_1, ..., X_{np}, v_1, ..., v_{np}]^T \]

If we see seek to solve the system for \( \mathbf{X} \) iteratively through Newton’s method, the equation for the residual has the form:
\[ R(\mathbf{X})^{t+1} = 0 \]
(5.18)

Linearizing the residual
\[ R(\mathbf{X})^{t+1} \approx R(\mathbf{X})^v + \frac{dR(\mathbf{X})}{dX} \delta \mathbf{X}^{v+1} \]
(5.19)

According to [5, 26], linearization of the full set can be expressed in the subsets as follows:
\[ R(\mathbf{X})^{t+1} = \begin{cases} R(X_p)^{t+1} \\ R(X_s)^{t+1} \end{cases} \]
(5.20)

\[ R(X_p)^{v+1} \approx R(X_p)^v + \frac{\partial R_p}{\partial X_p} \delta X_p^{v+1} \]
\[ R(X_s)^{v+1} \approx R(X_s)^v + \frac{\partial R_s}{\partial X_s} \delta X_s^{v+1} \]
(5.21)

In [5, 26], the primary set of variables is a function of both \( X_p \) and \( X_s \), while the secondary set depends only on the secondary variables. For this reason, using the chain rule, the derivative of the primary residual can be expressed as:
\[ \frac{\partial R_p}{\partial X_p} = \frac{\partial R_p}{\partial X_s} \frac{\partial X_s}{\partial X_p} + \frac{\partial R_p}{\partial X_p} \]
(5.22)

From this scheme, all the derivative can be computed with the exception of \( \frac{\partial X_s}{\partial X_p} \). However, in an overall molar formulation, the equation from the secondary set are assumed to be locally converged in each Newton iteration [26] which yields to:
\[ dR_s(X_p, X_s) = \frac{\partial R_s}{\partial X_s} \frac{\partial X_s}{\partial X_p} + \frac{\partial R_s}{\partial X_p} = 0 \]
(5.23)
Therefore, as explained in [5], with an aid of the inverse theorem, the derivate of the primary variables with respect to the secondary can be computed from:

\[
\frac{dX_p}{dX_s} = -\left(\frac{dR_s}{dX_p}\right)^{-1} \frac{dR_s}{dX_s}
\]  

(5.24)

This way, the full Jacobian can be computed to solve the system:

\[
\delta X^{v+1} = -J_{Total}^{-1} R(X)^v
\]  

(5.25)

\[
J_{Total} = \begin{bmatrix} J_p \\ J_s \end{bmatrix} = \begin{bmatrix} \frac{dR_p}{dX_p} & \frac{dR_p}{dX_s} \\ \frac{dR_s}{dX_p} & \frac{dR_s}{dX_s} \end{bmatrix}
\]  

(5.26)

5.2 Chemical models

In addition to the regular transport models, in-depth water diversion requires additional information on how to build the chemical reactions and how to generate the permeability changes. From a chemical point of view, literature provides two main reaction for silica gelation. The two equations described by [24, 9] are:

\[
H_4SiO_4(aq) + H_4SiO_4(aq) \stackrel{k_1}{\rightarrow} H_8Si_2O_7(gel) + H_2O
3 \text{ components reaction}
\]  

(5.27)

\[
H_8Si_3O_{10}(aq) + H_4SiO_4(aq) \stackrel{k_2}{\rightarrow} H_8Si_4O_{12}(gel) + 2H_2O
4 \text{ components reaction}
\]  

(5.28)

It is important to highlight that as the equation differ, difference are also expected for the rate of reaction values \(k_1\) and \(k_2\).

Regarding permeability estimation, two options include a regular Carman-kozeny relation and a permeability relation based on a pore throat blockage presented by [1]. The Carman-Kozeny permeability can be present as:

\[
k(\phi) = C \frac{\phi^3}{(1 - \phi)^2}
\]  

(5.29)

In the previous equation \(C\) is a constant relating grain diameter and tortuosity \((C = D^2_p/\tau)\).

The pore-throat blockage can be described as:

\[
k(s) = k_o \left(1 + 275Y S_w^2 \frac{k_o}{\phi_o}\right)^{-2}
\]  

(5.30)
where \( Y \) represents the mass fraction of deposited silicate over the mass of water.

Referring to porosity, the variations for all the models will be accounted through the molar deposition of the solid species as follows:

\[
P V = V_{\text{cell}} - V_{\text{rock}} - V_{\text{solids}}
\]  

(5.31)

Diving by the cell volume to include porosity:

\[
\phi(t) = 1 - k_{\text{rock}} - \frac{V_{\text{solid}(t)}}{V_{\text{cell}}}
\]  

(5.32)

In terms of moles of solid species produced:

\[
\phi(t) = 1 - k_{\text{rock}} - \frac{N_{\text{solid}}(t) \times M_{\text{v, solid}}}{V_{\text{cell}}}
\]  

(5.33)

where \( k_{\text{rock}} \) correspond to the fraction of volume corresponding to rock which remains unchanged in time, \( N_{\text{solids}} \) the mole of solid species deposited and \( M_{\text{v, solid}} \) the molecular volume of the solids in \([\text{m}^3/\text{mole}]\).

Combining all the alternatives, there are four options for the water diversion process.

![Figure 5.2](attachment:figure.png)

**Figure 5.2:** Modeling alternatives for 2 permeabilities and 2 reactions scenarios

The evaluation and selection of the models is discussed in the following section.
5.3 Analytical vs numerical solution

To validate any numerical implementation, the numerical solution is usually compared with the analytical. However, the tested model is too complex and no analytical solution is available for it. The chemical transport module in Stanford’s AD-GRPS has substantially been tested in studies by [26, 22]. Nevertheless, this module was slightly adapted to represent the sodium silicate reaction.

The close-system kinetic reactor is considered as the analytical model. In this way, the molar variation of species can be evaluated without the influence of flow terms. The solution for this system can be found analytically by variable separation and direct integration of equation 4.3. Rearranging the terms of equation 5.27, silica’s gelation is reduced to:

$$2Si_{(aq)} \rightarrow k Si_{(gel)} + H_2O$$

(5.34)

Therefore, the rate of transformation for aqueous Silica from equation 4.3 can be formulated in the following terms:

$$\frac{dC_{Si_{(aq)}}}{dt} = -kC_{Si_{(aq)}}^4$$

(5.35)

where \(C\) stands for the concentration of silicate over time and \(k\) represents the reaction rate.

Translation to a molar base implies diving by pore volume as follows:

$$\frac{1}{PV} \frac{dM_{Si_{(aq)}}}{dt} = -\frac{k}{PV^4} M_{Si_{(aq)}}^4$$

(5.36)

where \(PV\) is the pore volume and \(M\) the number of moles in time.

This transformation allows direct comparison with the numerical solution from the simulator in molar form. Separating variables and integrating gives the analytical solution presented below.

$$M_{Si_{(aq)}}(t) = \frac{PV}{\sqrt[3]{3k} \sqrt[4]{t} + A}$$

(5.37)

In this equation \(A\) represents the integration constant that can be computed from initial conditions.

$$M(0) = Initial \ moles = \rho_w Z_{Si} PV$$

(5.38)

where \(\rho_w\) and \(Z_{Si}\) stand for water phase molar concentration and aqueous silicate overall molar fraction.

The final equation reads

$$N(t) = \frac{PV}{\sqrt[3]{3k} \sqrt[4]{1 + \frac{1}{3k(\rho_w Z_{Si_{(aq)}})^4}}}$$

(5.39)
Using this solution, the numerical approximation can be checked and the error generated from different time discretization can be assessed.

5.4 Model calibration

Two calibration studies will be described below. The first will be used to match the results of core scale experiments, while the second will be used to reproduce data from previous studies at the reservoir scale.

Core experiments by [28], where silicate was injected to produce a permeability reduction, are a convenient dataset for calibration. The calibration parameter is the rate of reaction. First, experimental values of this parameter provided by [9, 1] will be tested. Later, the parameter will be adjusted to provide the best fit to experiments. The results will be compared with core-scale experiments from literature.

For the reservoir scale, a 1D model will be used to test all four different mechanisms of reservoir blockage presented in section 5.2. Starting from parameters by Hiorth, the rate of reaction will be adjusted to provide a blockage. The modified kinetic rate will be compared with experimental results. Judging from results at the core and reservoir scale, a single model will be selected to run 2D and 3D scenarios, and the application to the channels and geothermal studies.

Foreseeing the need for additional grid refinement due to the kinetics terms, a sensitivity study in space and time will be implemented. To test the convergence of results, the moles of solid silicate will be traced for different grid sizes and simulation time steps.

5.5 Reproduction of previous studies

Having selected a single model with the appropriate resolution, the simulation conditions presented in [1], will be reproduced for the 2D and 3D hierarchies. Although some differences are anticipated because of the more accurate solution methods, it is expected that generalities of the solution will be comparable. The simulation results will be contrasted in terms of production rates and total oil recovered. Furthermore, the results of the blockage will be compared regarding plug size, plug permeability and total volumes of silicate used. Discussion of the differences will be presented, highlighting major concerns and solution for future work will be proposed.

To reduce simulation time on the 2D and 3D models, two strategies are implemented based on the section 5.4. First, the simulation step will be adapted according to the
process taking place. Second, conditions from flow (pressure, saturation, temperature, etc.) will be used as initial condition to feed reactive flow.

As previously discussed, the reactive transport involves different physics at separate scales. Kinetic reactions, such as gelation of silica, are represented by local equations taking place in much shorter times than transport. Accounting for this, the overall simulation process can be divided into three sections, shown in the following graph:

![Diagram](image)

**Figure 5.3:** Time step discretization according to process. The red line corresponds to the moles of solid silicate produced.

Since the reaction process produces changes on a small period of time, see moles of solid silicate in red on the figure above, this section will be run with a refined time step. For the sensitivity study, we will be using the restart option as shown in Fig 5.3.

## 5.6 Practical applications

This section presents how the in-depth divergence approach will be tested in sections 6.7 and 6.8 for two applications on a more realistic reservoir structure - one for the channelized hydrocarbon reservoir and another for the low-enthalpy geothermal reservoir.

In a channeled reservoir, the approach will be simulated to investigate the capability of blocking more realistic and complex geometries and improve the sweep efficiency of the waterflooding process. The reservoir includes high and low permeability zones with a 5 spot well pattern. The results of flow deviation will be assessed based on the saturation map and production rates.
In the geothermal application, the method is simulated to delay the thermal breakthrough of cold water and increase the lifetime of the geothermal doublet. The water diversion process is expected to recover additional energy from the subsurface formation by deviating the flow path between injection and production wells. The results of the process will be assessed through the temperature map and the temperature of the production well.
Chapter 6

Results

This chapter details the solutions of simulations in different scenarios. First, a validation of the chemical module against the analytical solution is presented. Afterwards, the model is tuned with core experiments. Then, the results from a case study by [1] are presented and compared with results of our models. Moreover, a sensitivity analysis is carried on the chosen model. The chapters ends with two applications: one for a channelized subsurface and another for a geothermal well doublet.

6.1 Analytical vs numerical solution chemical model

Below we present the comparison of the analytical solution from equation 5.39 with the results from simulation. The main assumptions is no-flow condition, known as a closed reactor system.

Figure 6.1: a. Analytical vs Numerical solution for dt of 1 day. b. Error for different time steps
The proposed numerical approximation gives a good fit with the analytical solution. Even for a highly nonlinear relation, order four reaction rate, the error rounds 10% in the transient zone and is close to 1% in steady state conditions. From the error plot, a clear relationship can be observed between the time discretization and the error.

![Error order](image)

**Figure 6.2: Loglog plot for global error approximation**

The logarithmic plot of the error vs time steps shows that the linear regression gives almost 1 to a power fit. Recapitulating the error concepts from section 4.3, the first order character, \( O(h^1) \), with respect to time discretization of the global error can be confirmed.

### 6.2 Calibration with core experiments

In order to compare and calibrate the models presented in figure 5.2 with experimental data at ambient temperatures, it is important to normalize the rate of reaction in equation 4.4 with respect to the thermal component.

\[
k = \frac{1}{a\xi e^{\beta[HCL]}c^\gamma \sqrt{[Ca]} e^{\frac{E_b}{RT}}}
\]

\[
k = k_o e^{-\frac{E_b}{RT}}
\]

\[
k_o = \frac{k}{e^{\frac{E_b}{RT}}}
\]

(6.1)

In the equation (6.1), \( k_o \) represents the part of the reaction rate dependent solely on chemistry of the solution. From the results of Icopini and Hiorth at ambient temperature for silicate gelation in bulk conditions at 0.16w% and 4w%, \( k_o \) values are:
Normalized reaction rate $k_o \ [mol/m^2]\cdot s^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>Icopini</th>
<th>Hiort</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$2 \cdot 10^4 - 6 \cdot 10^7$</td>
<td>$1 \cdot 10^{12}$</td>
</tr>
</tbody>
</table>

Table 6.1: Reaction rates from experiments in bulk at 25°C for concentrations of 0.16w% silicate in Icopini’s and 4w% silicate in Hiorth’s experiments.

Introducing Hiorth’s $k_o$ values to the models to replicate experimental results performed by the same author in Berea cores with continuous injection of 4w% silicate, generates the following results:

![Graphs showing mobility reduction RF over time for different models compared to core experiments using reaction rate by Hiorth.](image)

**Figure 6.3: Modeled scenarios compared to core experiments using reaction rate by Hiorth**

In Fig.6.3, the mobility reduction RF is defined as initial permeability over final permeability ($k_o/k_f$). Observations from the plots indicate that models 2 and 4 (permeability by pore throat blockage) don’t follow the behavior of the core experiments. On the other hand, models using regular Carman-Kozeny permeability give a closer
match with the experiments.

When the reaction rate is adjusted for each model to provide a better fit with experimental results, we observed the following trends:

Comparing simulations results (see Table 6.2 below) with the reaction rate values described in the literature, it can be observed that the models 1 and 3 (Carman-Kozeny correlation) have values of half and a third of the magnitude reported by Hiorth. On the contrary, in models 2 and 4 (pore throat blockage), the required rates are two orders of magnitude lower.

This order of magnitude difference can be explained by the kinetics in a void space and in a porous bulk. As the gridding for the core geometry provides very resolved mesh, the concentration term (prescribed as moles per volume) becomes larger giving a better match with 4w% concentration experiments from Hiorth. This suggests the need of upscaling this parameter when comparing bulk and core scale experiments. To
gain more insight of this parameter, a sensitivity analysis is presented in the following section.

<table>
<thead>
<tr>
<th>Model</th>
<th>$k_\alpha$</th>
<th>Icopini</th>
<th>Hiorth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$6.0 \cdot 10^{11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$4.0 \cdot 10^{10}$</td>
<td>$2 \cdot 10^4 - 6 \cdot 10^7$</td>
<td>$1 \cdot 10^{12}$</td>
</tr>
<tr>
<td>3</td>
<td>$3.4 \cdot 10^{11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$4.0 \cdot 10^{09}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2: Fitted reaction rate values in contrast with values from experiments in bulk at 25°C for concentrations of 0.16w% silicate in Icopini’s and 4w% silicate in Hiorth’s experiments.

### 6.3 Simulation results from 1D

This section aims to gain insight into the behavior of the reaction’s kinetics, more specifically about the reaction rate $k$ from equation 5.35. For this purpose, the thermal and chemical part of this parameter are addressed, emphasizing on how the reaction is greatly driven by the thermal part.

From equation 6.1, the reaction rate can be divided into:

$$k = \left( a_\chi e^{[HCL]} e^{\gamma \sqrt{|C|}} \right)^{1} \cdot e^{\frac{-Ea}{RT}}$$

$$k = k_{chemical} \cdot k_{thermal}$$

The chemical part, $k_{reaction}$, relates how fast the reaction occurs to the eyes of parameters in the silicate solution such as the ionic strength, pH, salinity and buffer concentration, etc. A practical approximation for this parameter is presented in equation 4.4 from [1]. As discussed in the previous section, this parameter has a wide range of values spread through several orders of magnitude depending on the composition of the silicate solution, table 6.2.

Tests on a 1D geometry (1D version of the reservoir in app A) show that an overestimation of this parameter can lead to a premature activation of the reaction and a near-wellbore damage. On the other hand, underestimation of the reaction rate can lead to a reduced blockage or more than necessary silicate injected.
Fig. 6.5 describes the variations in permeability due to changes in the reaction rate. From left to right in the figure, the first image shows an ideal $k$. The middle image depicts effects of overestimating the reaction rate. Lastly, the picture on the right reveals the permeability results of underestimating this parameter.

The thermal part plays a major role in the kinetics of the reaction in this model. As the silicate solution is advected in the subsurface, it will experience a thermal shock as it crosses the thermal front which travels much slower. It is expected that crossing from a colder to warmer zone gives the fluids enough energy to trigger the reaction and form a plug. This series of events are portrayed in Fig. 6.6 where the moles of the silicate in solution decreases while crossing the thermal front.

In conclusion, a successful calibration of the reaction rate should satisfy three conditions. First, it should lay near the values proposed in the literature. Second, it should avoid near-wellbore damage. Finally, it should allow for a thermal activation of the reaction while crossing the thermal front.
6.4 Time and space resolution

Transport and kinetics are phenomena involving very different physics. From the governing equations 4.12 and 5.35, it is noticed that transport is a global equation while kinetics is a local one. For this reason, the highly nonlinear scale dependency is expected in this model.

The space and temporal domains for the transport phenomenon have been broadly studied. Consensus is observed for the convergence of the solution with grid blocks of several tenths of meters and simulation steps in the order of weeks or even months. In contrast, reactive transport is known to generate faster effects in smaller domains. For this reason, the characteristic numbers for time and spatial scales are not expected to hold.

To determine a proper time and space resolutions over which a converged solution can be assumed, a time-space convergence study is implemented below. The study is performed for a 1D subsurface with kinetic rate following the fourth model (see section 6.2). The convergence of the results can be assessed by the number of total mineral silicate moles present in the plug.

![Figure 6.7: Space and time resolution for 1D simulation with the kinetic rate from the fourth model](image)

By increasing the resolution in space and time, the solution converges at a relatively fine time and spatial scales. However, very high resolution is not viable for 2D and 3D problems due to the prohibitive computational time. Therefore, a time step ranging from 1 to 2 days giving an error below 3% seems appropriate for larger models. Concerning space, a spatial grid with character size of 1m along flow direction also produce an error below 3% and is appropriate for a multi-dimensional simulation.
6.5 Kinetic rate

In this section, the model will be calibrated for a 1D subsurface, having the reaction rate as a modifiable parameter. The calibration is performed to provide an effective in-depth blockage of the reservoir. Moreover, the results from the proposed models are compared between each other and contrasted against results from other studies.

6.5.1 Calibration of kinetic rate

In [1], Hiorth et al. propose a homogeneous idealized reservoir where they tested in-depth water diversion. In order to compare those results with our approach, the same reservoir geometry is used. While Hiorth at al. present results from a 3D model, their reservoir is scaled to 1D and 2D respectively for each section. The characteristics of the reservoir and other parameters are given in appendix A.

For the injection of 4w% silicate, the reaction rates and injected volumes are:

<table>
<thead>
<tr>
<th>Model</th>
<th>(k_{\text{rxn}} \text{ [mol/m}^3\text{s}]^{-1} \cdot \text{s}^{-1})</th>
<th>Volume [m(^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1.0 \cdot 10^7)</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>(4.0 \cdot 10^6)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(1.0 \cdot 10^7)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(4.0 \cdot 10^6)</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3: Normalized reaction rates that create a blockage for each model

From the Fig. 6.8, it is noticed that Models 1 and 3, are not able to produce a significant change in the permeability profiles in order to produce a water diversion. With the given values for silicate injection and reaction rate, a minimum permeability of 3000 mD is reached on model 3. This number will not allow a significant portion of water to flow in the lower permeability layers as it is 6 times larger than the values in these zones. Therefore, modeling permeability through a regular Carman-Kozeny is not a suitable approximation and suggest that blocking the entire pore space can become very costly in terms of silicate injection.

Looking at results from models 2 and 4 in Fig. 6.8, a sharp permeability reduction is observed. The permeability reaches values of 500 mD or lower, allowing a diversion of flow to the initially lower permeability areas. These results suggest that the use of a permeability reduction model from equation 5.30, base on blockage of the pore throat only, is sufficient for flow diversion. For this reason, model 4 (four species reaction with pore-throats permeability reduction) will be used for further multi-dimensional...
From table 6.3, the test of the four models on a simple 1D reservoir demonstrates that the reaction rate used to match the core experiments in the previous section (within the range suggested by Hiorth et al.), is no longer sufficient to produce a blockage in the middle of the reservoir. Instead, the reaction rate values are closer to the magnitude reported by Icopini.

The simulation results on 1D confirm the adjustment of the kinetic rate when the scale changes. While for core experiments in section 6.2 this parameter is in the order of magnitude of Hiorth’s studies, in the reservoirs scale it shows a trend towards the values suggested by Icopini. The main difference between the experiments is the silicate concentration. It is 4 weight % in Hiorth et al. study and 0.16 weight% in the Icopini’s study.
Looking back to the grid size for both scenarios, the core model accounts for cells in the order of 0.5 mm, while the reservoir’s grid is in the order of 1m per block (2000 times difference). In the numerical model, the concentration is calculated by dividing the moles in each cell by its pore volume. This means that increasing the block size is nearly equivalent to a dilution of concentration. This explanation matches our observations where a small scale model accounts for the reaction rate of the high concentration experiment, while the reaction rate for a larger scale models gives a better match for a low concentration experiment.

These results indicate the necessity for a better experimental and numerical study of the process as well as the development of appropriate upscaling technique for both kinetic description and the reactive flow.

6.5.2 Sensitivity to the reaction rate

The reaction rate has proven to be a complex parameter difficult to match seeing its dependency to the scale. Earlier, this parameter was adjusted to fit the range proposed by Hiorth et al. We demonstrated that their experimental results matched better the reservoir scale. Here, the sensitivity of reservoir blockage due to variation of this parameter is studied by tracking the moles of solid silicate produced and permeability reduction.

The reaction rate was therefore variated over a ±50% range. The results on the permeability of the block and moles produced are shown below.
Figure 6.9: Sensitivity of mole of silicate produced and permeability due to changes in the reaction rate.

Figure 6.10: Effects on a. permeability profiles and b. solid Si moles produced due to perturbations in the reaction rate.

From figures 6.9 and 6.10, it is noticed that the variation over the moles of solid silicate is not very strong. On the other hand, the variations in permeability are stronger. It is important to trace changes of this parameter since it is directly responsible for changes in flow behavior.
6.6 Multi-Dimensional Models

6.6.1 2D simulation

This section includes the results of 2D modeling over the reservoir in [1]. The results include the formation of an in-depth blockage, water diversion, production rates and cumulative productions.

Results description

An injection schedule is presented in the Table 6.4. The simulation was performed for a 2000 days period with the injection of 4%w silicate. These conditions produce the permeability reduction and water deviation path around the plug shown in Fig. 6.11.

<table>
<thead>
<tr>
<th>Period [days]</th>
<th>Molar fraction (Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>$1 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>200</td>
<td>0.01 Si</td>
</tr>
<tr>
<td>1380</td>
<td>$1 \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

Table 6.4: Injection schedule for 4% silicate solution

It is observed that the model creates an effective blockage causing water to divert to the low-permeable zone. The plug size is about 200 meters long, spreading over...
the entire high-permeable channel’s width. The permeability in this section has been reduced to an average of 260 mD from original 4000 mD. Deposition of mineral silicate is also observed in small areas outside the main channel.

As shown by the streamlines in Fig. 6.12, the water has deviated to lower permeability zones giving a better sweep in these areas.

Figure 6.12: Water saturation with (a) and without (b) silicate injection.

The improvement in sweep efficiency is evident when the difference in saturation maps of the two simulations (with and without silicate injection) is plotted as shown in Fig. 6.13.

Figure 6.13: Water saturation profiles resulting from the $S_w$ of silicate injection minus $S_w$ from no silicate injection.

The water saturation distribution displays two important facts. First, the recovery in the later extremes of the reservoir is largely improved with water saturation close to
0.9. Second, a clear stable waterfront is created after crossing the plug which is an indication of a better sweep efficiency.

The production plots below illustrate the difference in oil recovery obtained during the process.

![Production rates and Cumulative production comparison between no silicate injection and after silicate injection model 4](image)

Comparisons between the base case and silicate injection, reveals that in-depth water diversion indeed improves oil recovery. From Fig. 6.14a, an increase in production rates occurs around 1000 days. This can be effectively attributed to the plug by tracing the moles of mineral silicate deposited over time, shown in Fig. 6.15.

![Moles of mineral Si deposited model 4](image)

Figure 6.15: Moles of mineral Si deposited model 4
silicate deposition shows the plug fully formed at around 1000 days. The small delay between the plug formation and the increase in oil production rate corresponds to the time it takes the newly swept oil to reach the producer well. From figure 6.14b, the total increment in production accounts for 6%, for a simulation period of 2000 days (7.5 years).

The most important simulation parameters and results are shown in the Table 6.6 below.

| Process parameters | | | | |
|-------------------|-----------------|-----------------|-----------------|
| Injected silicate | Plug Volume | Plug’s Permeability | Cumulative Oil |
| [m³] | [m³] | [mD] | increment |
| 3.4 · 10⁵ | 1.9 · 10⁵ | 260 | 6% |

Table 6.5: Process parameters for injection schedule of 4%w silicate solution

Comparison with Hiorth et al. results

Contrasting the results from [1] with the results presented in this document, a significant difference can be observed. Regarding the permeability distribution, Hiorth presents a solution that takes only 2 values, either 100% reduction or 0%. This kind of results seems to be strongly guided by the numerical implementation, used in [1], and their approximation procedure for a silicate deposition.

Addressing the blockage location, the model in [1] generates one blockage towards the producer’s end, while our results indicate the blockage much closer to the injector well. We observed that the position of the blockage is highly dependent on the
thermal front position, a condition that suggests differences in the treatment of the energy equation across Hiorth’s model and the one developed in our study.

Moreover, the blocked area size is substantially different. Results from [1] generate a blockage almost twice as larger in magnitude with a lower (almost by half) injected volume of silicate. Again, the difference in dispersion of silicate plug could have a major influence on the blockage size.

Another source of the difference can be attributed to the variations in the coupling strategy in two numerical implementations. Our simulation results indicate a significant coupling between flow, transport of mass, energy and chemical reaction. That advocates an implementation of a fully-implicit coupling in our framework. The model, described in [1], employs a loosely coupling strategy which is not sufficient to resolve the physical complexity of the process.

6.6.2 Sensitivity of 2D model

The sensitivity of the model resulting from variation of parameters including the concentration of silicate solution injected, the total volume of the silicate solution and the volume of upfront water batch, is presented in Fig. 6.17.

Overall, the variation of the additional total oil produced in all cases is quite moderate. Even the maximum variation of the parameters in ±50% won’t produced more than 2.5% difference in the additional recovery (2.23 × 10⁶ to 2.17 × 10⁶ m³). It is worth mentioning that the variations were obtained for each parameter independently. Therefore a positive variation of parameters can lead to further oil recovered. Moreover, even
a small variation over the total oil recovery is economically viable. Just a couple of percentage points over the base case (parameters from table 6.4) usually mean that the operation is reimbursed and extra benefit is obtained.

The improvements in oil production, suggested by the 2D simulation, may not address appropriately the potential of the in-depth water diversion approach. Next, we will present 3D simulation results where we expect that water generates a further sweep pattern around the blocked region which leads to even larger increase in oil recovery.

6.6.3 3D simulation

This section includes the results of 3D modeling over the reservoir in [1]. The results include the formation of an in-depth blockage, water diversion, production rates and cumulative productions.

For this section the same injection schedule and simulation times of section 6.6.3 are implemented (Table 6.4).

![Figure 6.18: a. Production rates and b. Cumulative production comparison between no silicate injection and after silicate injection model 4](image)

Comparisons between the base case and silicate injection for 3D, reveals that a further recovery is achieved and further complexities are present. From Fig. 6.18a, an increase in production rates occurs around 600 days. This value is closer to the time from Hiorth A.5 in Appx. A. This implies that the plug is created much earlier than in the 2D case. The reason being that by having more rock in 3D, more heat reaches the fluids and the thermal front moves slower. Moreover, a second water break through is observed around 1200. It is attributed to the water breakthrough taking place in
the other layers.

From figure 6.18b, the total increment in production accounts for 11%, at the end of the simulation period (7.5 years). Comparing this number with the amount reported in 2D there is an improvement of 5%.

The most important simulation parameters and results are shown in the Table 6.6 below.

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>Injected silicate $[m^3]$</th>
<th>Plug Volume $[m^3]$</th>
<th>Plug’s Permeability [mD]</th>
<th>Cumulative Oil increment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$3.4 \cdot 10^5$</td>
<td>$1.9 \cdot 10^5$</td>
<td>260</td>
<td>6%</td>
</tr>
</tbody>
</table>

Table 6.6: Process parameters for injection schedule of 4%w silicate solution

### 6.7 Application to Channeled subsurface

In the previous sections, we discussed the results of an in-depth diversion on an idealized reservoir. Although useful for assessing physics and testing results, is far away from the reality. Usually, the strategies employed in this scenarios don’t give the expected results for more complex geometries. To address these details, we performed the test in a more complicated reservoir structure.

The selected subsurface from [25] includes channels running diagonally on a square grid with two permeability contrast. The permeability in channels was assigned at 4000 mD, while in the riverbank region, the permeability was assigned at 50 mD. Further description of the reservoir can be found in appendix B.

For this subsurface, a 5-spots waterflooding pattern was implemented. Two producers with one injector in the middle are placed along channels. The other two producers are placed on the river bank, orthogonal to the channel’s direction. The corresponding well setup and permeability map can be found in Fig. 6.19.
The simulation was run for 1000 days. The injection strategy is described in Table 6.8. In both cases the injector well is controlled by Bottom Hole Pressure (BHP).

<table>
<thead>
<tr>
<th>Without silicate injection</th>
<th>silicate injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period [days]</td>
<td>Molar fraction (Z)</td>
</tr>
<tr>
<td>1000</td>
<td>1 $H_2O$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.7: Injection schedule for 4%w silicate solution.

The results of simulation can be seen in Fig. 6.20 and Fig. 6.21. The plots show that the production of the wells along the direction of channels (producer 1 and 3) is improved after the injection of the silicate. The production of the wells perpendicular to the direction of channels remains almost the same. The effect of the silicate injection can be observed around 600 days.
The effect of the permeability blockage is visible on the permeability and corresponding streamline distribution in Fig. 6.22. In this image, the silicate reduced the channel’s permeability at an average of 85% (4000 mD to 530 mD). This blockage makes water divert to the exterior of the channels providing a better sweep of this zone.
The total oil produced from the base case to the silicate case (table 6.8) increases from $5.20 \times 10^5$ to $5.67 \times 10^5$ $m^3$ over the field’s life. This represents an overall 9% increase in the total production. Evidence of this additional recovery is visualized in the water saturation and streamline plots from the image below, where a better sweep is identified especially around producers 1 and 3.
Figure 6.23: Difference in saturation from base case and silicate injection

Figure 6.23 depicts that the additionally recovered oil comes from the loves connecting the wells. This pattern shows a radial geometry suggesting that the silicate plugs changes the main linear flow pattern of the high-permeable channel to the one observed here. Additional figures from appendix support this conclusion.

In general, results from injection of silicate show that the changes in the permeability profile lead to flow diversion. The changes in the flow pattern around the plugs create a better sweep and contribute with additional oil from the regions between the wells. Furthermore, even if the plugs generated don’t reduce the high-permeable channels permeability to the values of the riverbanks, water diversion is still possible. Finally, a 9% increment in produced oil is a very attractive figure. Optimization of this application is likely to give even more interesting values.
6.8 Geothermal application

For the geothermal application, the purpose of the water diversion process is to create a blockage to delay the reduction in temperature of the production fluids. In principle, if water is diverted to unswept zones, the injection fluids will be in contact with the hot reservoir rock for a longer period. Therefore, by deviating from the main channels, the fluid will regain energy from reservoir rock and the thermal breakthrough will be delayed.

For this geothermal application, a single layer of the low enthalpy reservoir, typical for Western Netherlands and suggested in [31, 27], was modeled with a similar permeability contrast of 4000 mD for the channels and 500 mD for the floodplain. Further description of the reservoir can be found in appendix C.

![Permeability profile for geothermal doublet.](image)

According to [31], the geothermal well doublet stops being economical if the temperature of the produced fluids drops by 10 degrees from the original fluids. As for their estimation, this point is achieved close to 10 years after production, moment where the production well is shut down.

The injection schedule for the simulation is presented below. The control for the in-
jection well is a constant rate of 100 [m³/day]. This value is scaled according to the ratio between the original reservoir thickness and the thickness of the layer modeled in this study.

<table>
<thead>
<tr>
<th>Without silicate injection</th>
<th>silicate injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period [years]</td>
<td>Molar fraction (Z)</td>
</tr>
<tr>
<td>10</td>
<td>1 H₂O</td>
</tr>
<tr>
<td>1.4</td>
<td>0.01 Si</td>
</tr>
</tbody>
</table>

Table 6.8: Injection schedule geothermal doublet.

The temperature profile for the produced fluids over a period of 35 years for the base case and after water diversion is presented in Fig.6.25.

Figure 6.25: Production’s fluids temperature without and with silicate injection.

From the figure above, it can be observed that for the base case the temperature starts decreasing around 16. Beyond this point, a sharp decline is noticed. In this scenario, the geothermal doublet reaches its lifetime according to the economic conditions specified above by 22 years of production when the temperature drops to 360 K.
On figure 6.25, the injection of silicate is represented by the red line. For this scenario, the temperature starts declining only after 20 years of production. Moreover, the temperature decline presents a smaller slope. In this case, the geothermal doublet will reach its economical lifetime on year 26.5 when the temperature reaches the mentioned threshold.

More insight of the thermal difference can be obtained from the following figure.

![Temperature profile difference](image)

Figure 6.26: Thermal profile difference for silicate injection and base case at year 25.

Comparison between the temperature profiles difference at 25 years after production helps to visualize where the heat contributions are coming from. An additional reservoir cooling can be detected from the low permeability regions outside the channel near the injector well. Moreover, it is noticed that the new heat boards the created permeability reduction around 800 metres in x and 600 meters in y, see Fig. 6.27 for the permeability profile distribution. Finally, some additional heat is observed reaching the production well, explaining the temperature difference of 17 degrees of Fig.6.25.

In this geothermal application, injection of silicate creates changes in permeability profile that divert water. As consequence, water flows outside the high-permeable path and the fluids reach zones of the reservoir at initial temperate which in turn increases its temperature. As a result, in-diversion by injection of sodium silicate delays the thermal breakthrough extending the lifetime of the geothermal doublet.
Figure 6.27: Permeability and streamlines profiles for silicate injection in geothermal application
Chapter 7

Conclusions and Future work

This section summarizes the discussion from previous chapters and recalls ideas therein to draw conclusions and give answers to the hypothesis presented in the introduction. Silica polymerization is a complex process worthy of further research. A major difficulty is how to describe via a reaction the particle growth from monomers to polymers. The current models from Iler and Icopini address mainly the initial stages of the process not going into specifics about particles growth. This last topic plays a major role in in-depth diversion since the deposited particles size is a key parameter in the porosity-permeability reduction model. Evidence of this was the results from models 1 to 4 in Fig. 6.8 where the reaction with a larger particle size resulted in a larger permeability profiles modification, making the reaction by Icopini a better option for reservoir simulation. For future studies, it would be pertinent to integrate reactions that account for later stages of polymerization and particle sizes growth.

In the same line of thought, two permeability relation where studied. The first, a Karman-Cozeny formulation, proves not to be an appropriate description for this process. In this formulation, the permeability is updated based on the overall pore space, which is not necessarily the pore space allowing flow. As consequence, larger quantities of sodium silicate are necessary to produce permeabilities profile reduction. The second permeability formulation relates the surface area of the deposited solids to the area of the pore throats. Therefore, this formulation allows smaller porosity reductions in order to generate significant permeability profiles modifications. Even though this kind of relations seems to be the appropriate approach, the model could be tuned for a specific particles size in future studies. These results put in evidence the urgent need of experimental data that could lead to a more precise model calibration. A particular experiment, that could be implemented, is an injection of silicate in core at reservoir temperatures. This will allow for permeability reduction and calibration of thermal activation.
Addressing kinetics, this concept was approached from two perspectives: resolution and scale. The sensitivity study for space and time domain confirms the need for a higher resolution when modeling fast changing and localized process as silicate gelation kinetics. More precisely, grid sizes of 1 meters along flow along with 1 day time steps are suggested to reach the numerically converged solution. This resolution is highly demanding on computational power, reason why the sensitivity analysis resulted essential for selecting grid size and time steps for multi-dimensional simulations.

Referring to the reaction rate, although sensitivity to this parameter is small, it is the solely most important parameter in the model calibration. In the literature, a wide range of values varying in several orders of magnitude are available. Moreover, it was noticed that a particular range was fit for modeling experiments at pore scale, while a different one provides more realistic results at the reservoir scale. The main difference across the set was initial silicate concentration. Rates from Hiorth with high concentration match the core scale results, while low concentration reaction rates from Icopini’s are a more suitable option for reservoir scale simulations. This dependency on concentration open a door for studying volumetric upscaling of this parameter in the future research.

Comparison between the results by Hiorth and the results obtained in this study exhibit substantial differences. The variation in permeability profiles, flow patterns and thermal activation of the reaction in this study indicate a significant coupling between flow, mass transport, energy and chemical reaction. That advocates an implementation of a fully-implicit coupling to model this process. The model, described in [1], employs a loosely coupling strategy which is not sufficient to resolve the physical complexity inherent to the process.

The results for the channeled reservoirs application show that additional hydrocarbons can be recovered due to the better sweep around the plugs. The added amounts account for 9% increment in total oil recovered for a 5 well spot pattern. The geothermal application shows how this process can be used to modify thermal profiles the same way it is done for water diversion. This process allows for a thermal breakthrough delay of several years. Moreover, the temperature of the production fluids was maintained above the economic threshold for 7 additional years leading to an extended geothermal doublet lifetime. The implementation in-depth water diversion in the two applications show a great potential for this process. The improvements in oil recovery and extension of the geothermal doublet life are economically attractive. Further research on this process will prove highly valuable.
Bibliography


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Appendices
## Appendix A

### Hiorth’s simulation

#### Reaction 1

<table>
<thead>
<tr>
<th>Component</th>
<th>Type</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Oil Decane</td>
<td>142 [gr/mol]</td>
</tr>
<tr>
<td>C2</td>
<td>Water</td>
<td>18 [gr/mol]</td>
</tr>
<tr>
<td>C3</td>
<td>$H_4SiO_3$ Aqueous Silicate</td>
<td>96.1 [gr/mol]</td>
</tr>
<tr>
<td>S1</td>
<td>$H_6O_7Si_2$ Gel Silicate</td>
<td>91.4 [cm$^3$/mol]</td>
</tr>
</tbody>
</table>

Table A.1: Reaction’s 1 species

#### Reaction 2

<table>
<thead>
<tr>
<th>Component</th>
<th>Type</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Oil Decane</td>
<td>142 [gr/mol]</td>
</tr>
<tr>
<td>C2</td>
<td>Water</td>
<td>18 [gr/mol]</td>
</tr>
<tr>
<td>C3</td>
<td>$H_4SiO_3$ Aqueous Silicate</td>
<td>96.1 [gr/mol]</td>
</tr>
<tr>
<td>C4</td>
<td>$H_8Si_3O_{10}$ Aqueous Silicate</td>
<td>252.3 [gr/mol]</td>
</tr>
<tr>
<td>S1</td>
<td>$H_8Si_4O_{12}$ Gel Silicate</td>
<td>156 [cm$^3$/mol]</td>
</tr>
<tr>
<td>k</td>
<td>reaction rate</td>
<td>$4 \cdot 10^6$ [mol/m$^3$]$^{-1}$ · s$^{-1}$</td>
</tr>
</tbody>
</table>

Table A.2: Reaction’s 2 species
Phases description

**OIL**

\[
\begin{align*}
\rho_o & = 0.8 \quad [gr/cm^3] \\
\mu_o & = 1 \quad [cP]
\end{align*}
\]

*Liquid heat capacity coefficients in \([J/g \cdot mol \cdot K^n]\)*

<table>
<thead>
<tr>
<th>GPL</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-7.913</td>
</tr>
<tr>
<td>2</td>
<td>0.9609</td>
</tr>
<tr>
<td>3</td>
<td>0.9609</td>
</tr>
<tr>
<td>4</td>
<td>1.131e-7</td>
</tr>
</tbody>
</table>

*Vaporization enthalpy*

HVR 5579 \([J/g \cdot mol \cdot K^{\text{ev}}]\)

*Heat conductivity*

THC 13 \([kJ/m \cdot \text{day} \cdot K]\)

**WATER**

\[
\begin{align*}
\rho_w & = 1 \quad [gr/cm^3] \\
\mu_w & = 1 \quad [cP]
\end{align*}
\]

*Liquid heat capacity coefficients in \([J/g \cdot mol \cdot K^n]\)*

<table>
<thead>
<tr>
<th>GPL</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.243</td>
</tr>
<tr>
<td>2</td>
<td>1.924e-3</td>
</tr>
<tr>
<td>3</td>
<td>1.055e-5</td>
</tr>
<tr>
<td>4</td>
<td>-3.596e-9</td>
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</tbody>
</table>

*Vaporization enthalpy*

HVR 4820 \([J/g \cdot mol \cdot K^{\text{ev}}]\)

*Heat conductivity*

THC 58 \([kJ/m \cdot \text{day} \cdot K]\)

Table A.3: Phase properties

**Corey relative permeability**

\[
\begin{align*}
\bar{n}_w & = 2 \\
S_{rw} & = 0.081 \\
k_{rw} & = 1 \\
n_o & = 3 \\
S_{rw} & = 0
\end{align*}
\]

Table A.4: Corey relative permeability parameters
### Rock description

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (φ)</td>
<td>0.3</td>
</tr>
<tr>
<td>Permeability (k)</td>
<td>4000 or 500</td>
</tr>
<tr>
<td>Compressibility</td>
<td>$10^5$ [1/bar]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>3000 [kJ/kg·K]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>$10^2$ [kJ/m·day·K]</td>
</tr>
</tbody>
</table>

Table A.5: Rock properties

### Reservoir description

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>x</td>
<td>2400  [m]</td>
</tr>
<tr>
<td>y</td>
<td>600   [m]</td>
</tr>
<tr>
<td>z</td>
<td>70    [m]</td>
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<tr>
<td>Cells in x</td>
<td>480   -</td>
</tr>
<tr>
<td>Cells in y</td>
<td>30    -</td>
</tr>
<tr>
<td>Cells in z</td>
<td>7     -</td>
</tr>
<tr>
<td>Depth</td>
<td>4000  [m]</td>
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<tr>
<td>Pressure</td>
<td>400   [m]</td>
</tr>
<tr>
<td>Temperature</td>
<td>370 [K]</td>
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</table>

Table A.6: Reservoir parameters

### Well placement

<table>
<thead>
<tr>
<th>Well</th>
<th>X [m]</th>
<th>Y [m]</th>
<th>Perforation in Z [m]</th>
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</thead>
<tbody>
<tr>
<td>Producer</td>
<td>405</td>
<td>300</td>
<td>4030 - 4040</td>
</tr>
<tr>
<td>Injector</td>
<td>1995</td>
<td>300</td>
<td>4030 - 4040</td>
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</table>

Table A.7: Well coordinates

Figure A.1: Hiorth’s reservoirs initial permeability profile
Figure A.2: Hiorth’s Final permeability reduction factor RF

Figure A.3: Hiorth’s final water saturation distribution without silicate injection

Figure A.4: Hiorth’s final water saturation distribution after silicate injection
Figure A.5: Production rates without and with silicate injection Hiorth
Appendix B

Channels

<table>
<thead>
<tr>
<th>Reservoir description</th>
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</thead>
<tbody>
<tr>
<td>x 1300 [m]</td>
</tr>
<tr>
<td>y 1300 [m]</td>
</tr>
<tr>
<td>z 10 [m]</td>
</tr>
<tr>
<td>Cell in x 10 -</td>
</tr>
<tr>
<td>Cell in y 10 -</td>
</tr>
<tr>
<td>Cell in z 1 -</td>
</tr>
<tr>
<td>Depth 4000 [m]</td>
</tr>
<tr>
<td>Pressure 400 [m]</td>
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<tr>
<td>Temperature 370 [K]</td>
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Table B.1: Channeled reservoir parameters

<table>
<thead>
<tr>
<th>Geothermal simulation</th>
</tr>
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<tbody>
<tr>
<td>Reaction:</td>
</tr>
<tr>
<td>Fluid properties:</td>
</tr>
<tr>
<td>Relative permeability:</td>
</tr>
<tr>
<td>Rock properties:</td>
</tr>
<tr>
<td>As per table A.2 in Appx. A</td>
</tr>
<tr>
<td>As per table A.3 in Appx. A</td>
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<td>As per table A.4 in Appx. A</td>
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Table B.2: Channeled reservoir simulation parameters
### Well placement

<table>
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<tr>
<th>Well</th>
<th>X [m]</th>
<th>Y [m]</th>
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<tbody>
<tr>
<td>Producer1</td>
<td>190</td>
<td>230</td>
</tr>
<tr>
<td>Producer2</td>
<td>900</td>
<td>350</td>
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<td>Producer3</td>
<td>1120</td>
<td>720</td>
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<td>Producer4</td>
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<td>630</td>
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<td>Injector</td>
<td>740</td>
<td>490</td>
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Table B.3: *Well coordinates in channels*

---

Figure B.1: *Saturation maps. a. No Silicate injection. b. After Silicate injection.*
Appendix C

Geothermal

<table>
<thead>
<tr>
<th>Reservoir description</th>
</tr>
</thead>
<tbody>
<tr>
<td>x 1800 [m]</td>
</tr>
<tr>
<td>y 1200 [m]</td>
</tr>
<tr>
<td>z 10 [m]</td>
</tr>
<tr>
<td>Cell in x 180 -</td>
</tr>
<tr>
<td>Cell in y 120 -</td>
</tr>
<tr>
<td>Cell in z 1 -</td>
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<tr>
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<tr>
<td>Pressure 400 [m]</td>
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<tr>
<td>Temperature 370 [K]</td>
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Table C.1: Geothermal reservoir parameters

<table>
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<th>Geothermal simulation</th>
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<tbody>
<tr>
<td>Reaction: As per table A.2 in Appx. A</td>
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<td>Fluid properties: As per table A.3 in Appx. A</td>
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Table C.2: Geothermal Simulation parameters

<table>
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<tr>
<td>Well</td>
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<tr>
<td>Injector</td>
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</table>

Table C.3: Well coordinates geothermal

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