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Coupling Reactive Transport with Discrete Fracture Modeling for Subsurface Energy Applications

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ABSTRACT

Mineral precipitation can significantly impact the permeability of fractures within geologic reservoirs crucial for carbon sequestration, geothermal energy, and oil/gas production. This thesis aims to (1) provide a comparative overview of existing experimental insights and simulation techniques for modeling such reactive transport processes in fractured geologic media, and (2) develop discrete fracture network (DFN) models that are coupled to reactive transport to enable simulating how fracture permeability changes during mineral precipitation events, In the first objective, I summarize our current understanding of mineral precipitation in fractures based on recent experimental results and demonstrate the utility of DFN models for simulating reactive transport involving mineral precipitation, including simulations tied to lab or field data. In the second, a DFN model coupled to the reactive transport code PFLOTRAN is developed to enable the simulation of precipitation and permeability within a physically and chemically simplified DFN consisting of two minerals, where gypsum dissolves and calcite precipitates. This thesis lays important groundwork for future research to better understand the complicated roles of mineral precipitation on fracture flow in a host of subsurface energy applications.

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Chapter 1

Introduction

Fractures are critical components in subsurface reservoirs utilized for energy production or storage. In low-permeability reservoirs that lack sufficient pore connectivity to transmit fluids, flow is restricted to fractures or channels. In cases where a fluid is intended to be contained underground, such as for storage of energy (e.g., natural gas) or a waste product (e.g., CO_2 or wastewater), a low-permeability reservoir serves as an overlying seal or caprock, and fractures within this seal are detrimental to storage operations. In general, fractures are susceptible to significant changes in their ability to transmit fluids due to chemical reactions resulting either from natural processes or directly from the extraction or injection of fluids for various engineering operations. Understanding how fractures, and flow within them, evolve due to geochemical reactions under reservoir conditions is critical to maintaining or preventing fluid transport through fractures in a host of reservoir engineering applications. In particular, it is important to understand how fluid transport changes as minerals in the host rock dissolve, and/or as new minerals precipitate.

Fractures are important to unconventional oil and gas production, where hydraulic fracturing techniques are employed to stimulate (i.e., generate fractures) in a tight reservoir to generate sufficient permeability for hydrocarbons to be extracted. Maintaining this induced fracture permeability is critical to maintaining hydrocarbon production rates, which can be hindered by detrimental processes like the formation of mineral scale. Scale refers to the precipitation of solid minerals, either from fluid mixing or fluid-rock interactions; these minerals can clog wellbores or tubulars, equipment, and the formation itself, inhibiting fluid flow.

Previous studies have shown that barium sulfate (barite, $BaSO_4$) scale is problematic in the Marcellus shale (Jew et al., 2018; Li et al., 2018), and can form when surface waters rich in sulfate are mixed with produced waters containing barium during initial well stimulation operations (Xiong et al., 2020). Mineral scale has also been shown to be problematic to geothermal energy production in reservoirs where fluids are circulated through fractures to produce heat that can be extracted and converted to power at the surface (Scheiber et al., n.d.).

Conversely, mineral precipitation is often desirable during geologic CO_2 storage (GCS), where mineral trapping of injected CO_2 represents the most secure form of CO_2 trapping (Menefee et al., 2018). In certain geologies, CO_2-fluid-rock interactions lead to the conversion of injected CO_2 into solid carbonate minerals (e.g., $CaCO_3$, $MgCO_3$) within the pores or fractures of the host reservoir (Matter & Kelemen, 2009). Precipitating such solid minerals within a fractured reservoir inevitably can lead to permeability reduction, which can limit a reservoir's overall CO_2 storage capacity and efficiency by reducing the ability to continue injecting CO_2 (Luhmann et al., 2017). Understanding the relationships between mineral dissolution-precipitation and permeability change is critical for optimally engineering such reservoirs for maximum CO_2 storage without self-sealing.

In engineering endeavors where the focus is on fluid retention within a reservoir, such as in conventional oil/gas production or applications involving gas storage, permeability through fractures in overlying caprocks intended to seal the reservoir is undesirable. In particular, existing fractures or faults in intended caprock layers could preclude the use of reservoirs for CO_2 storage, where long-term retention of injected CO_2 is paramount (Vialle et al., 2019). Interactions among injected CO_2, fluids in the host reservoir, and the surrounding rock can lead

to the dissolution of minerals along fractures in caprocks, which in turn can lead to the widening of potential leakage pathways (Spokas et al., 2018). Experimental work has also demonstrated that the stress under which fractures are created has a substantial influence on their permeability, which controls whether or not they become leakage paths (Frash et al., 2017).

Overall, understanding the conditions under which minerals dissolve or precipitate, and the implications of such reactions for fluid transport, is critical to reservoir engineering. Of particular interest is preventing mineral precipitation in reservoirs susceptible to mineral scale buildup or inducing precipitation during CO_2 storage operations for mineral trapping of injected CO_2. However, the ways in which such reactions manifest and influence fluid transport throughout fracture networks remain unclear. This thesis seeks to contribute toward filling this critical knowledge gap through discrete fracture network modeling coupled with reactive transport. The primary objective of this thesis is to improve our understanding of how fracture permeability evolves due to coupled dissolution-precipitation reactions within fractured reservoirs.

Chapter 2

Literature Review

2.1 Impact of Chemical Reactions on Fracture Permeability

In the realm of geoscience research, understanding the intricate interplay between rock geometry, fluid infiltration, and ensuing chemical reactions is pivotal. In general, mineral dissolution can enlarge fracture apertures, such as the dissolution of carbonate minerals in acidic fluids, while mineral precipitation can reduce them (Deng and Spycher, 2019). However, mineral precipitation can lead to different effects on permeability and is particularly difficult to study in laboratory settings. A previous experimental study on geochemical reactions and fluid transport in low-permeability reservoirs was conducted by Menefee et al. (Menefee et al., 2020). They conducted triaxial direct shear experiments on shale cores with varying calcite content, where high-concentration $BaCl_2$ solutions were injected upon fracturing the samples to induce visible precipitation. The experiments demonstrated that barium carbonate ($BaCO_3$) precipitated quickly within fractures formed by the shearing of shale cores under subsurface conditions. The rapid formation of precipitates led to an 80% reduction in fracture permeability in the most reactive core, indicating that precipitates resulting from fluid-rock interactions can significantly obstruct fluid transport. Across all experiments, precipitation was localized within the fracture networks, concentrating in regions that were more heavily fractured due to shearing. The results demonstrated that precipitation depends on the reactive surface area, the mineralogy of the sample, and the specific fracture geometry.

A further study by the same group evaluated the influence of precipitation on permeability through a series of triaxial direct shear experiments on dual-mineral cores

containing anhydrite and dolomite (Carey et al. 2022). The experiments were conducted within a computed tomography (CT) scanner that enables X-ray imaging. A concentrated solution of $BaCl_2$ was introduced into the cores to induce mineral precipitation that could be visible in X-ray radiographs. The study found that the injection of fluid-rock interactions led to the precipitation of barium sulfate and barium carbonate minerals (i.e., barite/witherite) within the fracture system. Despite observed precipitation, the permeability of the fracture system changed little following the initial fracturing event. The authors attributed this finding to the fact that precipitation was confined to relatively stagnant flow regions, while more open regions sustained high flow rates. It was also concluded that the rate of dissolution of native rock minerals was a key factor in the precipitation process.

Overall, these experimental results highlight the important role of grain-scale mineralogy and flow pathways on precipitation and how it impacts fracture permeability, but further computational studies would be needed to fully explore these connections beyond scales that can be reasonably evaluated in the lab. The next sections explore the status of modeling techniques to better understand such reactive transport processes in fractured media.

2.2. Reactive Transport Modeling in Simulated Fracture Networks

Much work has been done to advance our ability to model reactive transport processes within geological fractures. Existing modeling techniques fall into three main categories: equivalent continuum models, dual or multiple continua models, and discrete fracture networks. The equivalent continuum models treat fractures and rock matrices as a unified entity with an adjusted permeability to account for the presence of fractures. The dual-continua models add an additional continuum for fractures (i.e., unique porosity-permeability relationships), which is in

union with the rock matrix continuum. Multiple continuum models expand upon dual continuum models by investigating additional co-located interacting media (Deng et al., 2019). Alternatively, discrete fracture network models explicitly represent individual fractures based on geometry (aperture, length, and orientation) (Hyman et al, 2015). These models thus can simulate flow through an actual fracture network but are typically more time-intensive to run.

The governing equations (continuity, momentum conservation, and mass conservation) behind these methodologies are divided into the pore-scale method and the continuum-scale method. Pore-scale models excel in detailing geometry evolution through mineral precipitation and dissolution by discretizing void spaces and tracking fluid-solid interfaces, while continuum-scale models utilize average variables over each grid cell in which the solid phase and void space co-exist (Deng et al., 2019). Understanding interactions between hydrodynamic processes, diffusion, and reaction rates in fractures is necessary for predicting fracture permeability changes and overall reservoir behavior. The following sections detail studies that have applied specific techniques for modeling reactive transport and/or permeability in fractures.

2.3. Assessing Effective Permeability through 2D and 3D Fracture Network Simulations

Other research has investigated the impact of fracture networks on the effective permeability of low-permeability porous media. The motivation behind this work came from observing abrupt increases in permeability when a triaxial core-flood experiment, similar to the tests presented in Section 2.2, was conducted on a Utica shale sample. To assess changes in effective permeability due to percolation, two different fracture network models are utilized. One of these is a two-dimensional fracture propagation model (HOSS) which simulates fracture formation under mechanical stress and mimics the Utica shale experiment. The other is a three-

dimensional discrete fracture network (DFN) model (DFNWORKS) that randomly generates static fracture networks based on the properties of the same Utica shale sample. The study confirms that abrupt increases in effective permeability can occur when fractures propagate and percolate through a low-permeability matrix. The magnitude of the jump can be influenced by the arrangement of fractures but more so by the differences in fracture and matrix permeabilities. When the difference in permeability of the fractures and matrix is small, the impact on effective permeability is insignificant. However, larger contrasts between fracture and matrix permeability lead to substantial jumps in effective permeability, where a power-law relationship is observed. The HOSS model shows that effective permeability increases slightly before percolation and then stabilizes post-percolation, and the 3D DFN model reveals a non-linear increase in effective permeability with fracture density after percolation occurs. The paper highlights the importance of the transition from non-percolating to percolating networks in terms of observed permeability values and scaling behavior, which is useful for simulating various subsurface systems, including those relevant to hydraulic fracturing, carbon sequestration, and geothermal energy extraction.

2.4. Discrete Dual Lattice Models

A previous study sought to better understand the interplay between fracturing and permeability in shale by integrating a discrete approach to both mechanical behavior and fluid flow. A discrete dual lattice model comprises two main components: a mechanical lattice model and a fluid transport lattice. The dual nature allows for the simultaneous simulation of both solid and fluid phases, which captures the interaction between mechanical fractures and fluid permeability in shale (Li et al., 2017). The mechanical lattice model is based on the Lattice Discrete Particle Model (LDPM), designed to mimic shale's granular internal structure. This

model captures the initiation, propagation, and coalescence of microcracks within the shale matrix. The transport lattice model is built upon the mechanical lattice and models fluid flow within shale. This model facilitates fluid mass transport through both uncracked and cracked regimes, effectively linking mechanical fracturing with changes in permeability.

Simulations of direct shear triaxial tests on Utica shale were conducted using this dual lattice model. The simulated effect of cracking on the overall permeability of shale qualitatively agrees with experimental data. It was concluded that apparent permeability increases significantly when localized fractures develop (Li et al., 2017). Additionally, the specimen's size impacts both the mechanical response and the measured permeability with larger specimens showing a more pronounced post-peak behavior and a different scaling of permeability. Localized fractures were observed during the simulations, and these fractures played a significant role in the increased permeability measurements. The research suggests that the localized fractures could be used to extrapolate the permeability of larger specimens from smaller ones, indicating that the model could potentially be used to predict the behavior of shale at different scales. The discrete dual lattice model introduced by Li et al. can be used in predicting the fracture-permeability behavior of shale as it captures the interactions between mechanical fracturing and fluid.

2.5. Resolving Reaction Rate Discrepancies in Fractured Media

Another challenge in reactive transport modeling, particularly in mineral reactions in fractures, is the discrepancy between reaction rates measured in the lab and those measured in the field. A prior study explored the discrepancy between laboratory and field measurements of geochemical weathering reaction rates in subsurface fractured porous media using dfnWorks

software (see Section 4) to generate an ensemble of 3D-DFNs and simulate reactive transport using the reactive transport code PFLOTRAN. The simulations included chemical reactions with spatially and temporally varying flow resistance within fracture planes. Quartz dissolution was modeled, and the study explored the impact of fracture network connectivity on transport and mineral dissolution rates. Fractures were created and meshed using the feature rejection algorithm for meshing (FRAM) technique. Flow in the fracture network was modeled using the Richards equation with a variable permeability field. Quartz dissolution was simulated over 5 million years, while permeability, porosity, and mineral surface area were updated in each cell based on the chemical reactions occurring. Importantly, the dissolution rate was computed using the commonly used linear Transition State Theory (TST), which presumes mineral precipitation follows the same reaction kinetics but reverse direction as dissolution.

These simulations revealed a significant discrepancy between the predicted rates from TST and the simulated apparent rates in fractured media. In particular, the study found that quartz dissolution primarily occurred in well-connected, advection-dominated regions (primary sub-networks) of the fracture network. Once these regions were depleted of reactive minerals, the dissolution process became transport-limited in less connected, diffusion-dominated areas (secondary sub-networks). This transition led to apparent dissolution rates orders of magnitude lower than those predicted by TST. The authors developed a geo-structurally based modification to the TST rate law, incorporating the network structure's influence on the flow field and reaction rates. This correction factor accounted for the reduced mineral surface area available for dissolution in the secondary network and the limitation imposed by transport through the interface between primary and secondary networks. The application of this correction factor

significantly reduced the discrepancy between the simulated apparent rates and the rates predicted by TST.

Overall, this recent study provides a consistent approach to predicting reaction rates in fractured subsurface environments. It suggests that geological structure is a primary factor in the discrepancy observed between laboratory and field measurements of geochemical reaction rates. The methods and results significantly advance the understanding of geochemical reactions in fractured porous media, and the integration of geological structures into the prediction of reaction rates offers a new perspective on reactive transport modeling. Further advancements could come from future research, building on this recent study, to evaluate similar discrepancies and upscaling in precipitation rates.

2.6. Impact of Asperity Geometry on Fracture Permeability

Many of the previous studies also evidenced the influence of fracture asperities on chemical processes and permeability. An asperity is simply a contact point between fracture walls. Zimmerman et al. presented one of the first studies exploring the influence of contact area geometry within rock fractures on their permeability (Zimmerman et al., 1992). The authors begin by establishing the governing principles of fluid flow through fractures and reference the nonlinear Navier-Stokes equations and Hele-Shaw flow for their analytical framework. The boundary-element method, a numerical technique ideal for solving problems governed by Laplace's equation in two dimensions, is also employed. The researchers then take analogue measurements using conductive paper to simulate the flow of electrical current around obstacles analogous to fracture asperities. This method's high precision in measuring electrical conductivities provides a reliable proxy for validating the fracture permeability models derived

from the boundary-element analysis. The study further extends its methodological versatility by incorporating effective medium theory.

The results of their overall experiment reinforce that the permeability of a rock fracture is primarily controlled by the geometry of its void space. Specifically, the fluid's path becomes tortuous due to contact areas (asperities) where the faces of the fracture are in contact. Permeability was found to be dependent not just on the amount of contact area but also on the asperity shape. The effective medium theory employed provided very accurate estimates for the permeability of fractures with circular or elliptical asperities. For elliptical asperities, the effective permeability is adjusted by a factor that depends on the ellipse's shape, with the aspect ratio being a critical parameter, and the results infer that elongated asperities lead to lower permeability. Irregularly shaped asperities, which are more representative of natural fractures, were also studied. These asperities resulted in a lower permeability compared to what Walsh's expression would predict for circular asperities.

Overall, the results of this study suggest that the permeability for fractures with irregular asperity geometry can be approximated using an equivalent aspect ratio derived from imagining the actual asperities to be ellipses with the same total area and perimeter. The study concludes that the effective medium theory can be applied to fractures with irregular geometries, but they should include adjustments for aspect ratio to achieve more accurate permeability predictions. The presence of asperities decreases the permeability below the value for unobstructed flow between parallel plates, highlighting the importance of the asperity geometry in determining fracture flow characteristics (Zimmerman et al., 1992). The results provide theoretical insight for

incorporating the influence of different asperity contact areas and geometries into permeability modeling, which are present in naturally fractured geologic media.

Chapter 3

Existing Research Gaps

3.1 Relevance of Previous Research

Previous studies have highlighted several critical aspects related to this field. I am particularly interested in research surrounding mineral precipitation-dissolution reactions and fracture permeability within subsurface reservoirs. The overarching goal is to significantly advance the comprehension of subsurface fluid dynamics, thereby contributing to the efficient and sustainable management of natural resources.

Experimental studies have demonstrated that the injection and flow of reactive fluids can lead to mineral precipitation reactions that impact fracture permeability in low-permeability rock cores. Notably, previous studies demonstrated that the spatial distribution of precipitation along fractures is a key factor influencing overall fracture system permeability. This is a key motivator of my thesis which seeks to model reactive transport and permeability evolution in discrete fractures.

The categorization of modeling approaches into equivalent continuum, dual or multiple continua models, and discrete fracture networks displays the complexity of representing reactive transport processes in geological fractures. This highlights the need for advanced DFN models that can accurately simulate the dynamic interactions between fluid flow, chemical reactions, and fracture permeability changes.

The integration of DFNGEN, DFNFLOW, and DFNTRANS within DFNWORKS demonstrated the utility of 3D modeling in simulating fluid flow and solute transport in subsurface environments. This framework is particularly relevant to my research, as it underlines

the importance of sophisticated modeling tools in understanding fracture networks and reactive transport.

Investigations into Utica shale highlight abrupt permeability increases can occur due to fracture network percolation, with a significant impact from the differential between fracture and matrix permeabilities. This finding directly informs my thesis, as it exemplifies the intricate balance between fracture development and effective permeability in low-permeability media.

The discovery of discrepancies between laboratory and field measurements of geochemical weathering reaction rates in fractured sheds light on the complexities in predicting reactive transport behavior. This gap between theory and real-world observations aligns with my thesis's aim to refine models for better predictive accuracy in subsurface environments.

The development of a discrete dual lattice model to simulate interactions between mechanical fractures and fluid permeability in shale provides critical context for my work. It emphasizes the importance of understanding how localized fractures influence permeability, a concept central to my focus on permeability evolution in fractured media.

Research showing rapid barium carbonate precipitation in carbonate-rich shales underlines the major role of fluid chemistry and rock mineralogy in fracture permeability. This study's findings about the localization of precipitation and its impact on permeability resonate with my thesis's focus on geochemical interactions within fractures.

Investigations into the effects of flow rates and fracture geometries on calcite precipitation patterns in fractured dolomitic limestone offer a comprehensive view of the factors influencing fracture sealing. This aligns with my thesis's exploration of how mineral precipitation can be modulated to either enhance or obstruct fluid flow in fractures.

The impact of asperity shape within rock fractures on permeability provides foundational knowledge for modeling fracture flow characteristics. The emphasis on asperity geometry's role in determining permeability is particularly relevant to my research, which seeks to incorporate realistic fracture geometries in permeability models.

3.2 Statement of Intent

While previous research has laid a rigorous foundation, there are critical areas where our current understanding remains limited. This thesis aims to address these gaps and contribute insights in the following areas. The first goal is advancing discrete fracture network models to incorporate mineral precipitation. As mentioned throughout Chapter 2, we lack as complete an understanding of precipitation reactions as we have of dissolution reactions. Building on existing methodologies, this research seeks to develop more refined DFN models that more accurately represent the intricate dynamics of mineral precipitation and dissolution within fracture networks. My approach integrates discrete fracture network modeling with reactive transport mechanisms. Outdated modeling techniques that ignore these features may be viewed as less accurate or flawed in their applications to what my thesis investigates. Another goal is to develop models that specifically allow the modeling of permeability evolution during precipitation events. Ultimately, the groundwork laid here and future studies building upon this research can provide meaningful results that can be related to diverse geological settings. This thesis will not only build upon the existing body of research summarized in Section 2 but also forge new paths toward improving our understanding and capability to model the complex phenomena of mineral precipitation and dissolution in fractured geological media.

Chapter 4

Methodology

4.1 DfnWorks

4.1.1 Overview

In the context of subsurface flow and transport phenomena, understanding the evolution of permeability within discrete fracture networks (DFNs) is crucial for various applications, including carbon sequestration, geothermal energy extraction, and hydrocarbon production. This chapter explores the role of dfnWorks, a parallelized computational suite developed at Los Alamos National Laboratory, in advancing our understanding of precipitation-induced permeability evolution in fractured geological formations. By combining experimental or contrived data with advanced modeling techniques, dfnWorks offers a powerful framework for simulating fluid-rock interactions and their impact on fracture permeability, thereby addressing key knowledge gaps in subsurface science. DfnWorks integrates cutting-edge meshing algorithms, high-performance computing techniques, and flow solvers to accurately capture the complexities of fractured media. At its core, dfnWorks leverages the concept of discrete fracture networks, representing fractures as individual geometric objects with specific properties such as aperture, orientation, and connectivity.

4.1.2 Innovations

As previously discussed in Section 2.2, discrete fracture network (DFN) models explicitly resolve the fractures. One particular form of DFN simulations that has been widely used is the comprehensive suite dfnWorks, which was developed by lead researchers at Los Alamos National Lab to model flow and transport within subsurface fractures using (DFN)

methodologies (Hyman et al., 2015). DfnWorks integrates three core components: dfnGen, dfnFlow, and dfnTrans. These components facilitate the creation of 3D discrete fracture networks, simulate fluid flow through these networks, and model solute transport, respectively. DfnGen employs the Feature Rejection Algorithm for Meshing (FRAM) to generate fracture networks adhering to specific geological parameters. DfnGen's meshing process, utilizing LAGRIT, results in high-quality meshes suitable for complex flow simulations. DfnFlow extends the functionality of dfnWorks by enabling fluid flow simulations within the generated networks. It utilizes PFLOTRAN, a massively parallel subsurface flow code, to solve flow equations on the unstructured mesh created by dfnGen. DfnTrans focuses on modeling solute transport using a Lagrangian approach. It reconstructs the velocity field based on Darcy fluxes obtained from dfnFlow and employs particle tracking techniques to simulate solute movement (Hyman et al., 2015). DfnTrans addresses the challenge of navigating particle trajectories through fracture intersections, employing a mixing model to represent the split flow at these junctions. DfnWorks is designed for high computational efficiency and scalability, which has been the main challenge in prior employments of DFN, allowing it to handle large networks spanning from millimeters to kilometers. DfnWorks is a significant advancement in the field of subsurface flow and transport modeling. Its ability to generate and mesh DFNs, simulate fluid flow, and model solute transport addresses the complex interplay of geological features in subsurface environments (Hyman et al., 2015).

4.1.3 Capabilities

Mesh Generation (dfnGen) is a fundamental aspect of modeling fractured media using dfnWorks. It produces high-quality meshes that accurately represent the geometry and

connectivity of fractures. These advanced meshing algorithms are capable of handling complex fracture networks with millions of fracture elements. By discretizing the domain into finite elements and explicitly representing fractures as discrete entities, dfnWorks enables researchers to capture details of fracture geometry and topology, essential for accurate flow and transport simulations. As previously mentioned, dfnGen utilizes the Feature Rejection Algorithm for Meshing (FRAM) methodology to stochastically generate three-dimensional DFNs. It combines this with the LaGriT meshing toolbox to create high-quality computational meshes that provide a conforming Delaunay triangulation suitable for high-performance computing solvers (Hyman et al., 2015).

Flow Simulation (dfnFlow) provides a suite of flow solvers tailored for simulating fluid flow within fractured media. These solvers utilize numerical methods such as finite element or finite volume discretization to solve the governing equations of fluid flow and incorporate the heterogeneous nature of fracture networks (Hyman et al., 2015). By accounting for fracture aperture variations, intersecting fractures, and fluid-rock interactions, dfnWorks can accurately predict fluid flow pathways and velocities within fractured formations. DfnFlow simulates fluid flow through the network using PFLOTRAN, a massively parallel subsurface flow and reactive transport finite volume code. It allows for the analysis of complex flow patterns in fractured networks.

Transport Simulation (dfnTrans) is the aspect of dfnWorks that uses particle tracking algorithms for modeling and simulating transport in fractured media. By simulating the advection and dispersion of particles within fracture networks, dfnTrans enables researchers to assess the migration pathways and retention mechanisms of contaminants, including precipitated

minerals. This capability is particularly relevant to the study of precipitation-induced permeability evolution, as it allows for the assessment of how mineral deposition impacts fluid flow and contaminant migration in fractured reservoirs. DfnTrans adopts a Lagrangian approach for simulating transport through the DFN to determine path lines and solute transport (Hyman et al., 2015). This component is crucial for understanding how substances move and disperse within the fracture network.

4.2 Terminal

The Terminal is an application designed to interact with the macOS operating system through a command line interface. Terminal requires inputting text commands or scripts to perform various tasks. It can be used to display the contents of a directory or run a script that automates certain tasks, like opening an application. In this study, I used Terminal to navigate between my local machine and Docker.

4.3 Docker

Docker is a platform that facilitates containerization and the Docker daemon, dockerd, handles Docker's essential objects like images, containers, networks, and volumes. The client, “docker” sends commands to the Docker daemon. Images are read-only templates with instructions for creating Docker containers and containers are runnable instances of these images. A typical Docker command like docker run pulls an image and creates a container. I utilized the desktop variation for macOS, but Docker works for Windows and Linux systems. Once the Terminal is open, the command “docker pull ees16/dfnworks:latest” can be used to establish the image within Docker. The image is called “ees16/dfnworks:latest.” As alluded to previously, the command “docker run -ti ees16/dfnworks:latest” will pull the image and create a

new container. Another useful command is “Docker run -ti -v /Users/mychalkearns/Desktop/dfnThesis/:/dfnWorks/work ees16/dfnworks:latest” which mounts a volume and enables outputs to be saved from Docker to your local machine. Some of the results of my data are outputted as .vtk files. VTK is a visualization library that is used to program the ParaView visualization software. ParaView is the default program to open .vtk files.

4.4 ParaView

ParaView is a data visualization tool that allows the simultaneous display of data in different views, allowing for easy comparison and analysis of separate variables. It offers a wide array of built-in filters and allows custom filters via a programming language such as Python. ParaView is particularly useful for its ability to automatically generate animations from files with multiple time steps. Animations can be exported in common video formats or as image sequences. For the sake of this paper, we will be analyzing images. I have utilized the desktop application for macOS, but ParaView runs on Windows and Linux as well. It supports various file formats and is a powerful tool for in-depth data analysis and visualization. Within ParaView, you have the option to visualize different variables. Our initial model only includes liquid pressure, permeability, and material. We set up the model to visualize a discrete fracture network with six fractures. In this example, the network has one fracture in the system with a higher permeability than the rest.

4.5 PFLOTRAN

The next thing that we wanted to do was set up chemistry in this PFLOTRAN card and start doing some sort of dissolution and then secondary precipitation. It was decided that gypsum dissolution and calcite precipitation would be a good start. So, we started with that and

essentially tweaked the model for different time steps to visualize how the system evolved. From here on out, we controlled the chemistry, evolution of the permeability in the system, and subsequent time steps within the PFLOTRAN run card. The simulation block tells the PFLOTRAN card what kind of flow it's going to try to solve. In our initial model for subsurface flow, it is running in the Richards mode. This corresponds to a fully saturated Darcy equation and steady-state conditions. In terms of the chemistry PFLOTRAN card which models gypsum dissolution and calcite precipitation, the simulation block is taken out of the steady state. The new mode of flow is transient because we have the dynamic evolution of the system as the chemical reactions occur. The discretization or grid block tells the card what kind of mesh to look for. This is made by dfnWorks and handed off the network to PFLOTRAN. The fluid properties block details values such as the diffusion coefficient. This can be adjusted for targeting a secondary Dom Kohler number or Peclet number. The material properties block controls the different materials within the system. Multiple materials can be evaluated by adjusting parameters such as porosity and density. For simplicity, our initial model was a single material with porosity based on the initial volume fraction of gypsum. The output block details what properties are dumped out into the .vtk file that is processed in ParaView. The chemistry PFLOTRAN card displays things like the total amount of gypsum or calcite in the system, permeability, porosity, and dissolution/precipitation rates. The time stepping block is where the length of the simulation and time steps are adjusted. For the boundary conditions block, we have an inflow and outflow boundary. For the initial PFLOTRAN model, external files essentially say which nodes are on which boundary, and this is determined by Dirichlet pressure conditions. With high pressure at the inlet and low pressure at the outlet, the card finds the equilibrium

pressure according to the permeabilities and flow rates. For the chemistry PFLOTRAN card, the flow rate is volumetric. There is a constant flow rate that's going through the system per every time step. The basics of the PFLOTRAN card are the mesh, the properties of each of the cells, the time steps, the output, and the boundary conditions. The chemistry one is more complicated and includes various blocks pertaining to chemistry.

Chapter 5

Results

While the majority of this thesis effort has focused on developing the code to incorporate mineral precipitation into dfnWorks, this section presents preliminary results. The network was created by making the PFLOTRAN card and then running dfnWorks through Docker to produce viewable networks in ParaView. Figure 1 displays the initial model that was contrived. The fracture network consists of six discrete fractures and properties such as permeability are the main parameter of interest. Stressing the heterogeneity of each fracture, individual properties can be assigned to each fracture (permeability is shown in Figure 1).

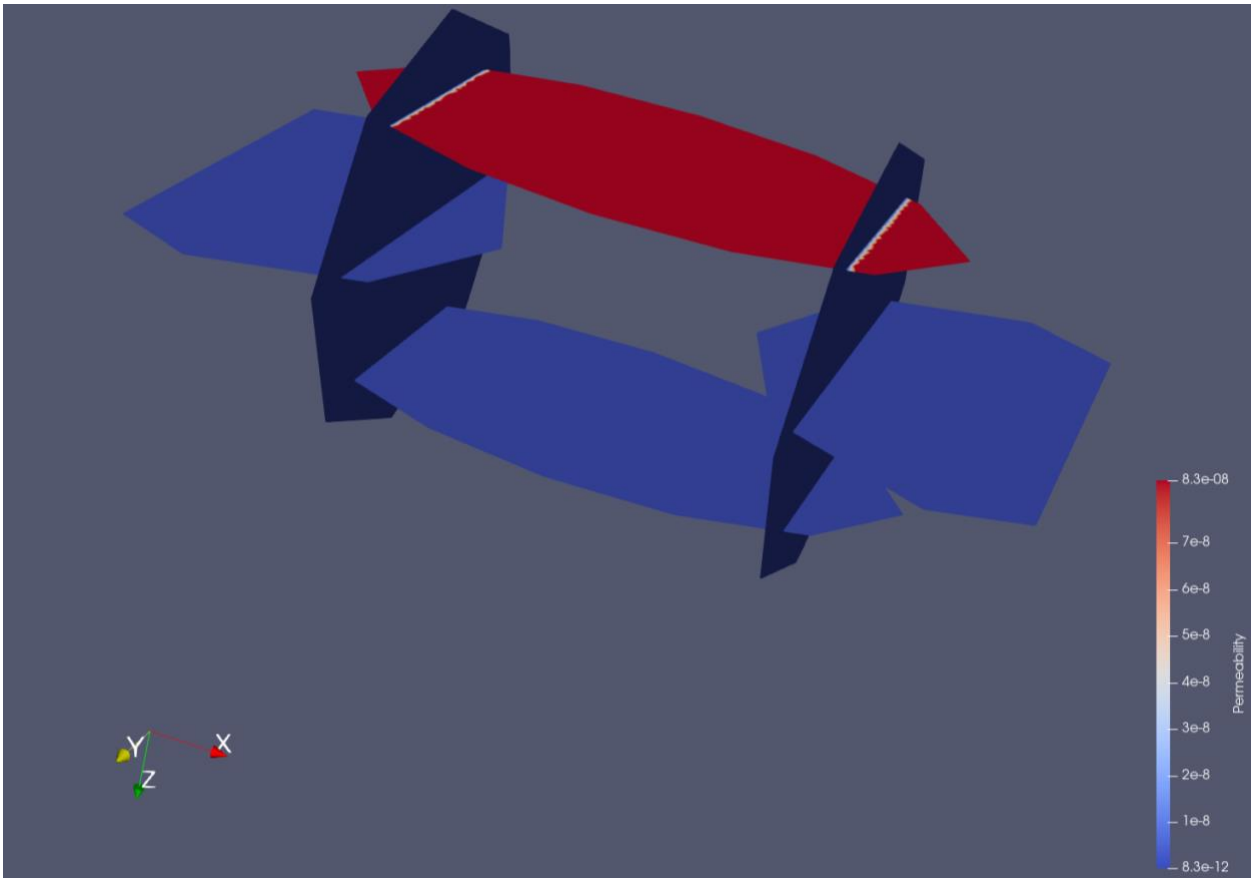

Figure 1. Initial model for discrete fracture networks (permeability)

The code was first simulated under the time conditions shown in Table 1 which equates to the span of one day. Figure 4 highlights the permeability of the fracture network as a result of the gypsum dissolution and calcite precipitation after one day.

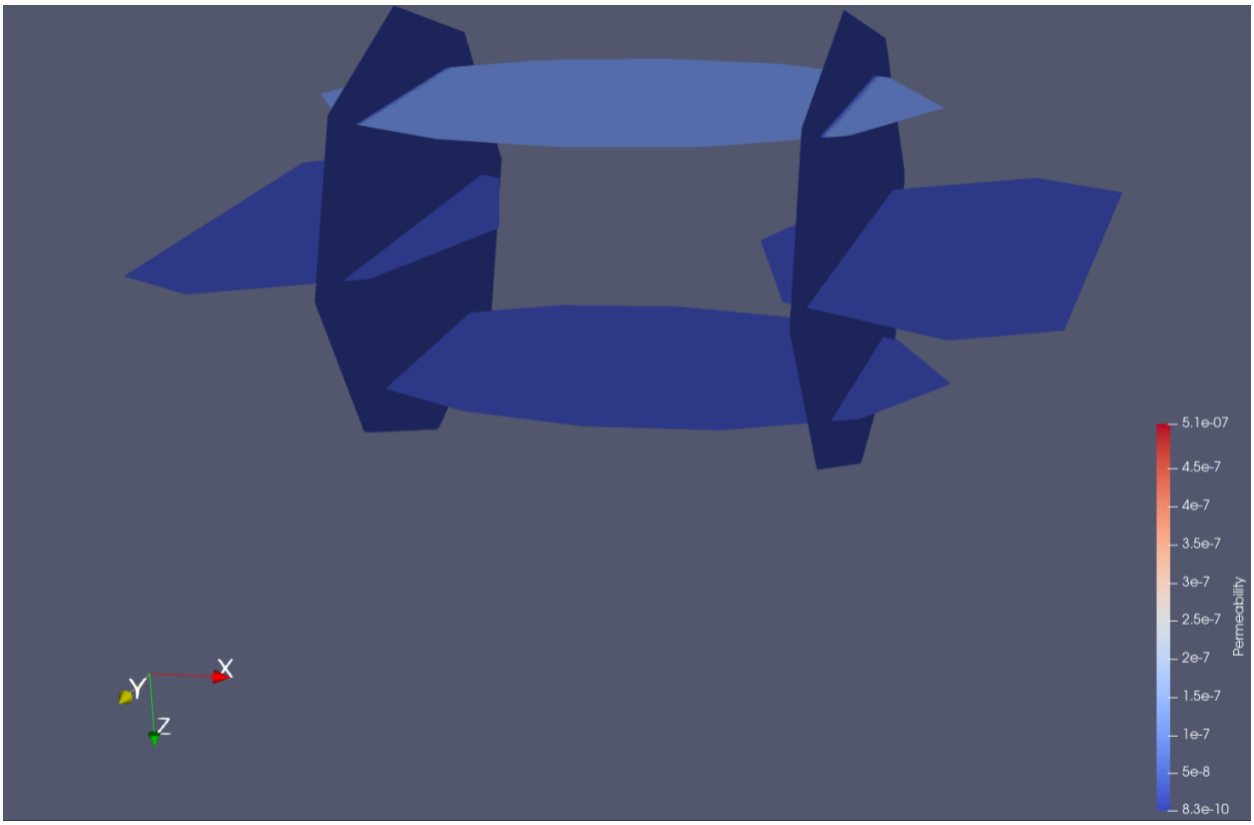

Figure 2. Chemistry model for discrete fracture networks (permeability at time = 0 days)

Figure 2 displays the same results but at initial conditions and Figure 3 displays the network after half a day. At initial conditions, one of the six fractures within the discrete fracture network is set to have a permeability of roughly three orders of magnitude greater than the remaining fractures.

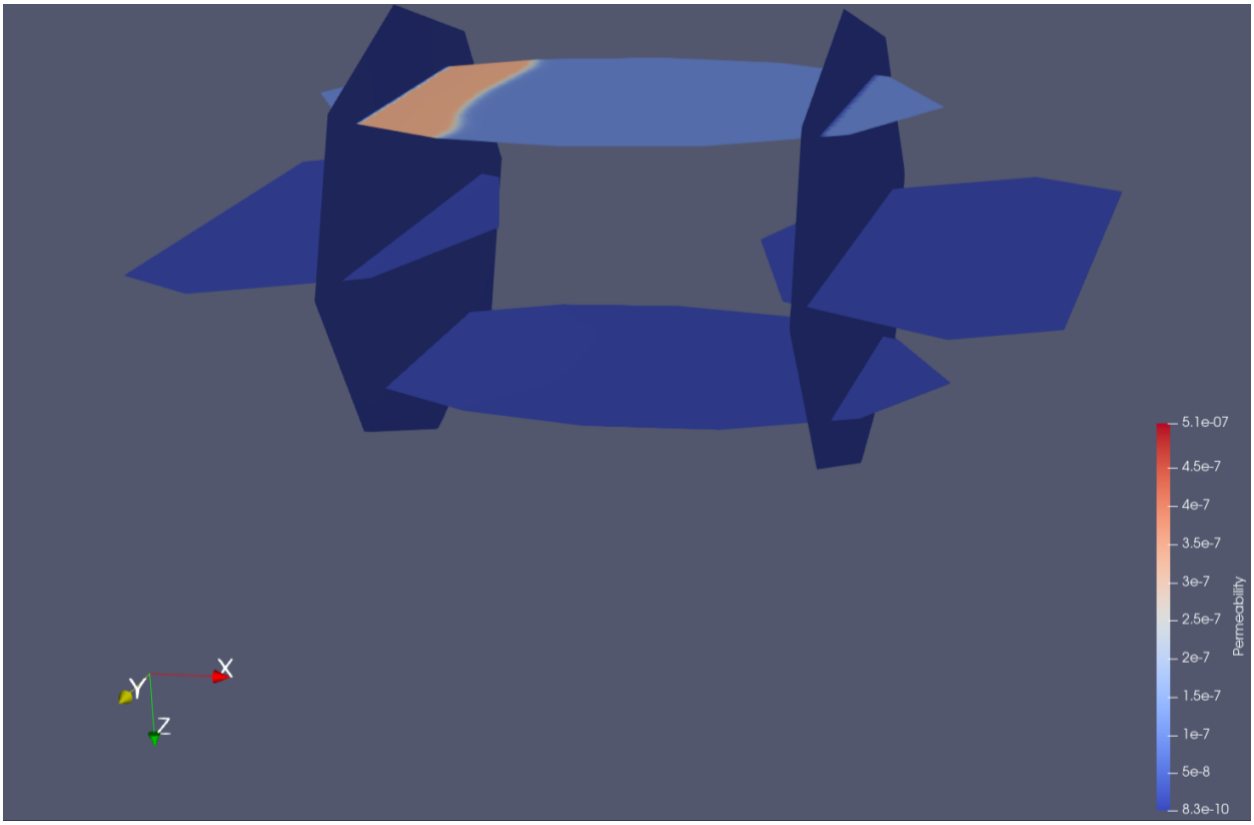

Figure 3. Chemistry model for discrete fracture networks (permeability at time = 0.5 days)

After just half a day, we can already observe that the volumetric flow rate has the greatest effect on the fracture with the largest initial permeability. The permeability is observed to increase at the inlet of fluid injection.

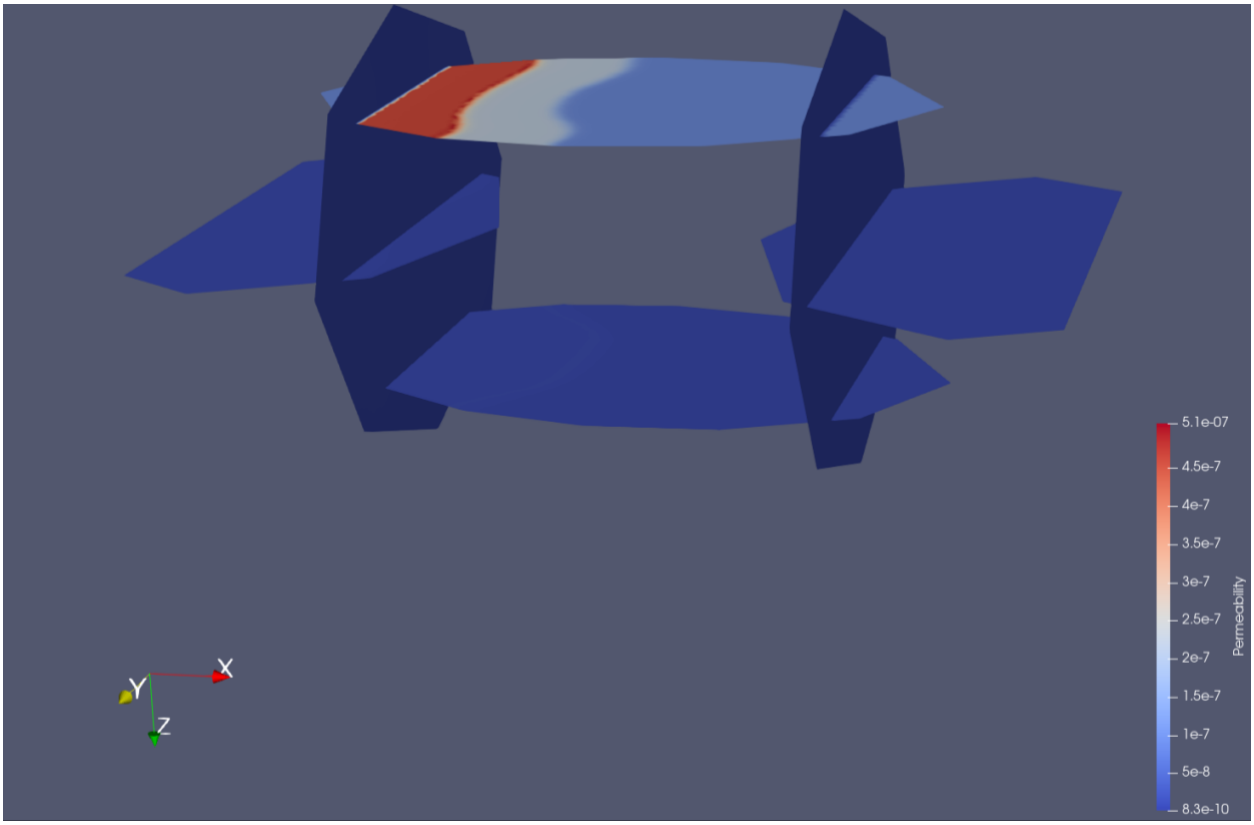

Figure 4. Chemistry model for discrete fracture networks (permeability at time = 1 day)

After one day of injecting, we concluded that the permeability is increasing in the x-direction where the fracture of the greatest permeability was located. To attempt to explain this phenomenon, one may view the chemistry output parameters within ParaView and find correlations between them and the permeability evolution. These are located in Figure 5 and Figure 6.

Table 1 briefly shows some of the variables that can be adjusted per each running of the PFLOTRAN card. A brief mention of other variables from the blocks mentioned in Section 3.5 include species and fluid concentrations, pH, liquid pressure, and temperature.

Table 1. Chemistry model variables for PFLOTRAN

Material Properties	*Value*	*Units*
Porosity	0.1	-
Density (Gypsum)	2305.15	kg/m^3
Mineral Kinetics	*Value*	*Units*
Rate Constant (Gypsum)	1.2d-8	mol/m^2-sec
Rate Constant (Calcite)	2.43d-5	mol/m^2-sec
Time	*Value*	*Units*
Initial Time Step	1.d-2	days
Final Time Step	1.d-2	days
Final Time	1.d0	days

Circling back to chemistry, it appears that our model is successful in modeling chemical reactions over time. If the porosity of gypsum is 0.1 (Table 1), then the initial volume fraction of gypsum at time zero would be 0.9. Figure 5 displays the volume fraction of gypsum after one day. It can be observed that the volume fraction of gypsum is decreasing at the injection inlet. This alludes to its dissolution, caused by the continuous injection of reaction-favoring fluid. After one day, the greatest fluctuation in the volume fraction of gypsum was 0.12, and this occurred in fractures closest to the inlet of fluid injection.

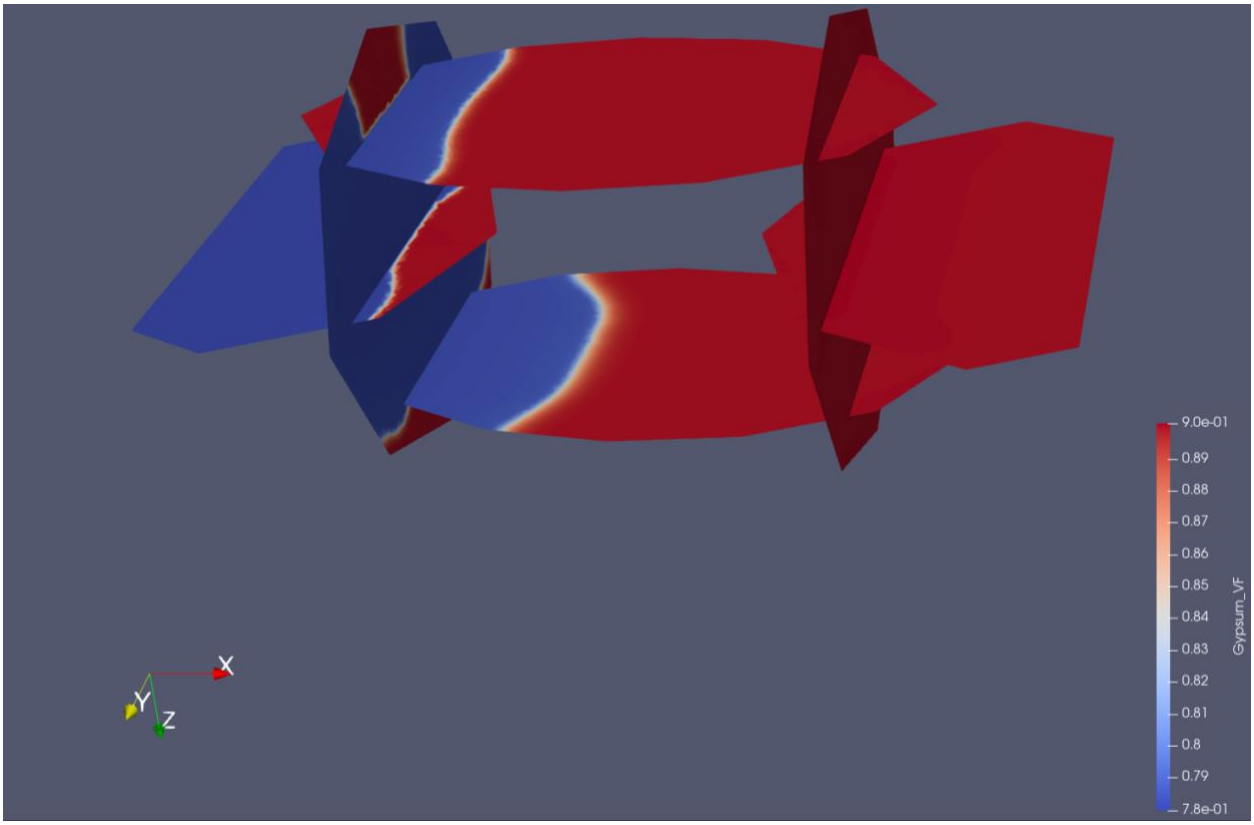

Figure 5. Chemistry model for discrete fracture networks (gypsum volume fraction at time = 1 day)

Calcite precipitation is still visibly observed after one day. In Figure 6, it is most clearly seen in the top and bottom fractures. The leftmost area of these fractures is a lighter shade of navy blue than the rest of the fractures in their rightward x-directions.

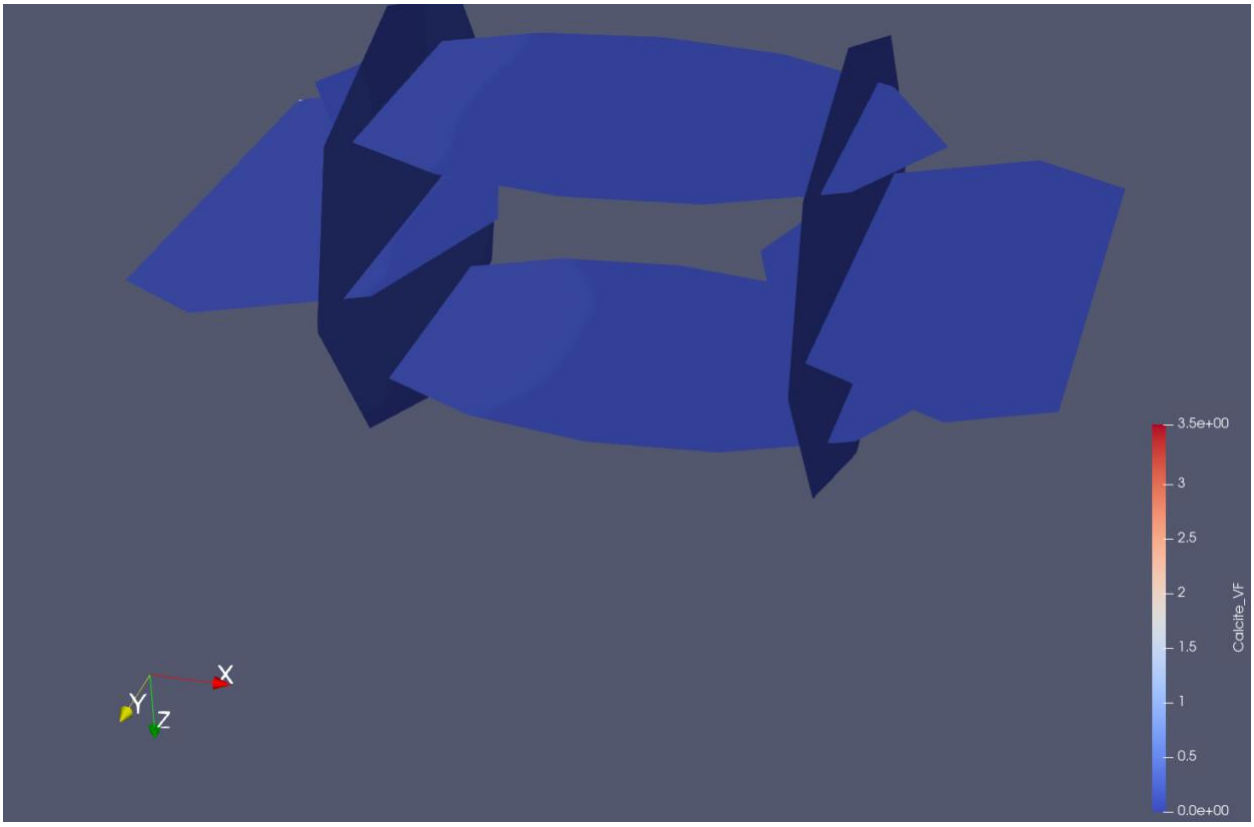

Figure 6. Chemistry model for discrete fracture networks (calcite volume fraction at time = 1 day)

After updating the PLOTRAN card to range from one day to one-hundred days the effects of reactive transport on the discrete fracture network are more visible. In Figure 7, the volume fraction of gypsum in most locations of the fracture is zero after only fifty days. The dark red colors highlight the location within the network where the volume fraction of gypsum is the same as the initial condition of 0.9.

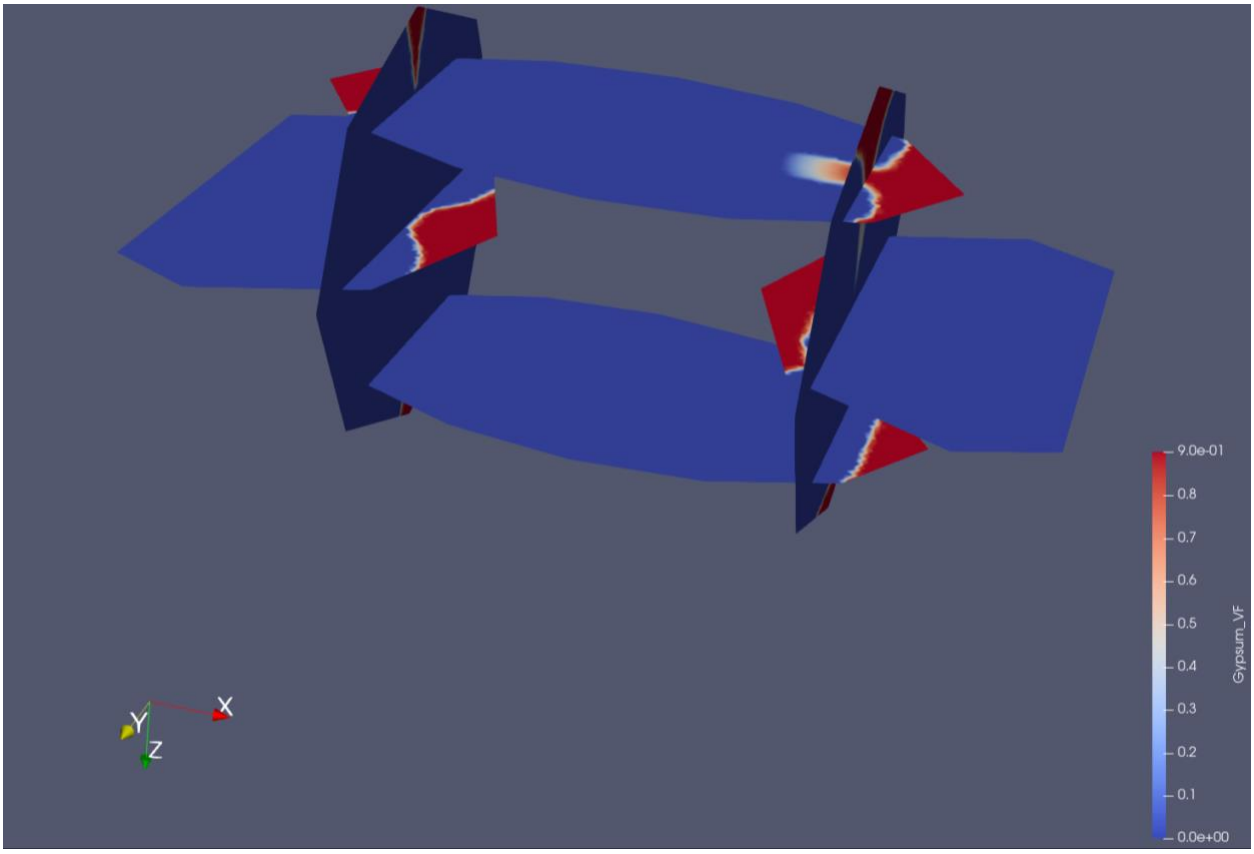

Figure 7. Chemistry model for discrete fracture networks (gypsum volume fraction at time = 50 days)

Similarly to Figure 7, calcite observed a significant increase in volume fraction after modeling the system for fifty days. Although the gypsum dissolution occurred relatively quickly as seen in Figure 5, the precipitation of calcite took longer. The volume fractions of calcite in Figure 8 display values majority in a range of 0.5 to 1. The color gradients are somewhat tricky to decipher except for the values that display a volume fraction of zero. These are the same locations in which gypsum dissolution failed to occur after fifty days.

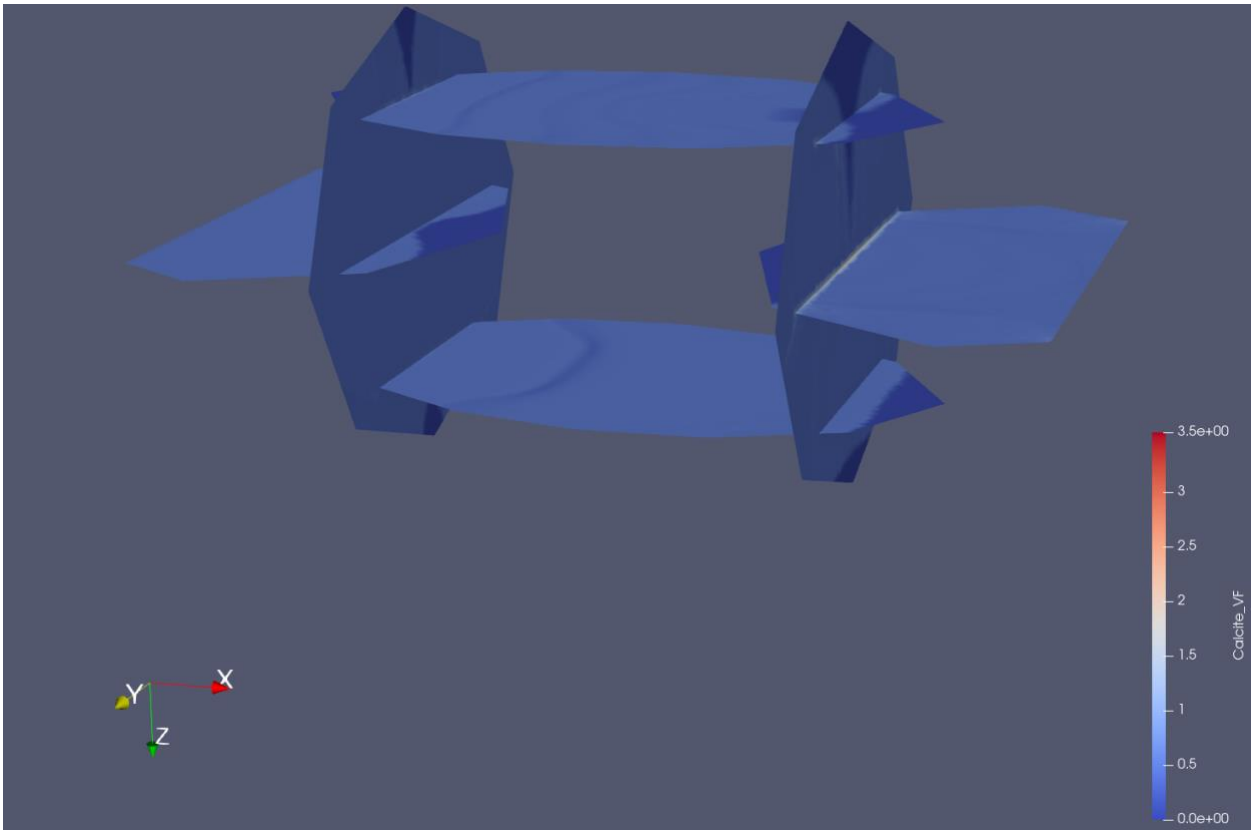

Figure 8. Chemistry model for discrete fracture networks (calcite volume fraction at time = 50 days)

One of the main objectives set out to be discovered by this thesis was the impact of mineral precipitation on the permeability of fracture networks. Figure 9 highlights the effects of the dissolution of gypsum and precipitation of calcite on the permeability after fifty days. Rough estimates of the permeability of the topmost fracture can be contrived. Based on the color gradients, it appears that the permeability of this discrete fracture increased fourfold due to the reactive transport after fifty days.

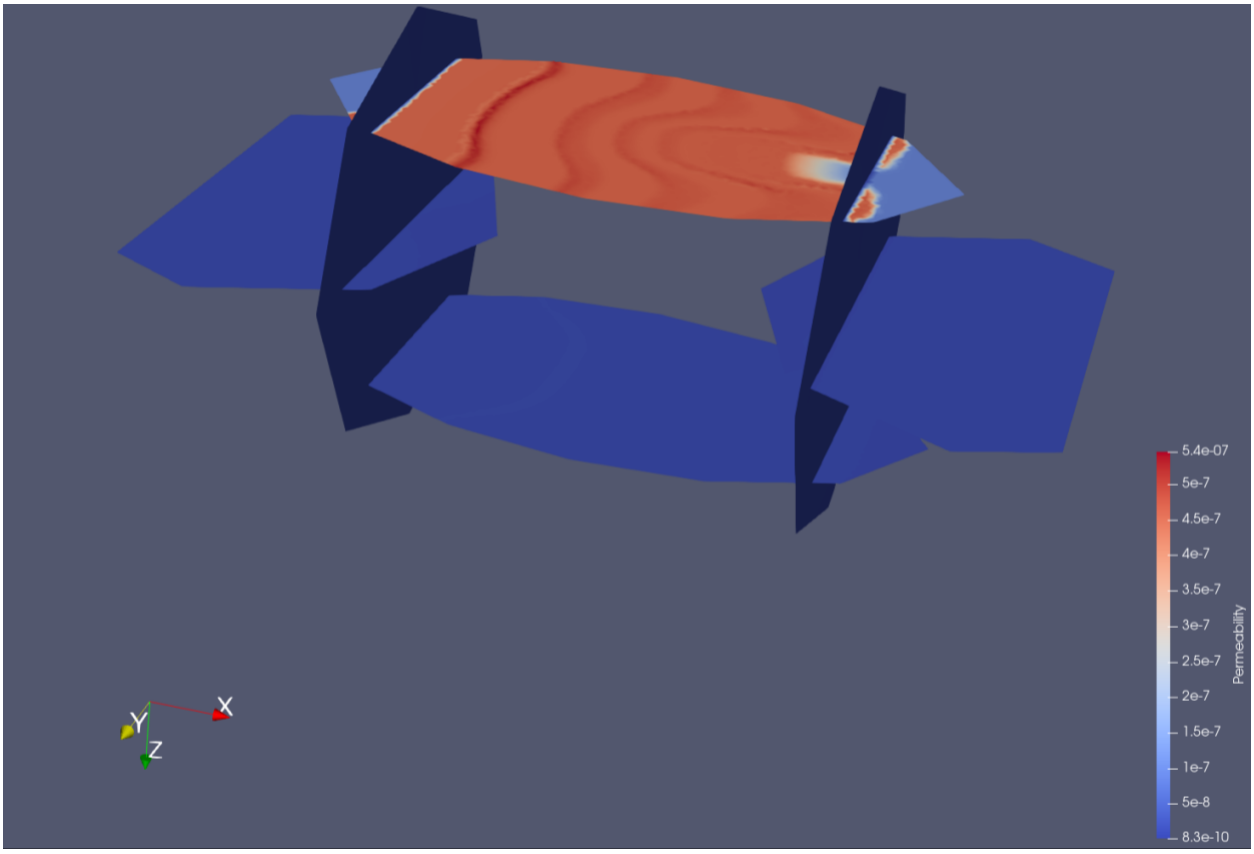

Figure 9. Chemistry model for discrete fracture networks (permeability at time = 50 days)

The last figure covered is Figure 10. This model displays the permeability of the discrete fracture network after 100 days. By comparing Figure 9 to Figure 10, it appears that the magnitude of precipitation for the topmost fracture did not change over the span of the additional fifty days. However, the increasing permeability trend propagates further along the x-direction with increasing time steps. This statement holds true for all times modeled by the discrete fracture network (initial conditions to one hundred days).

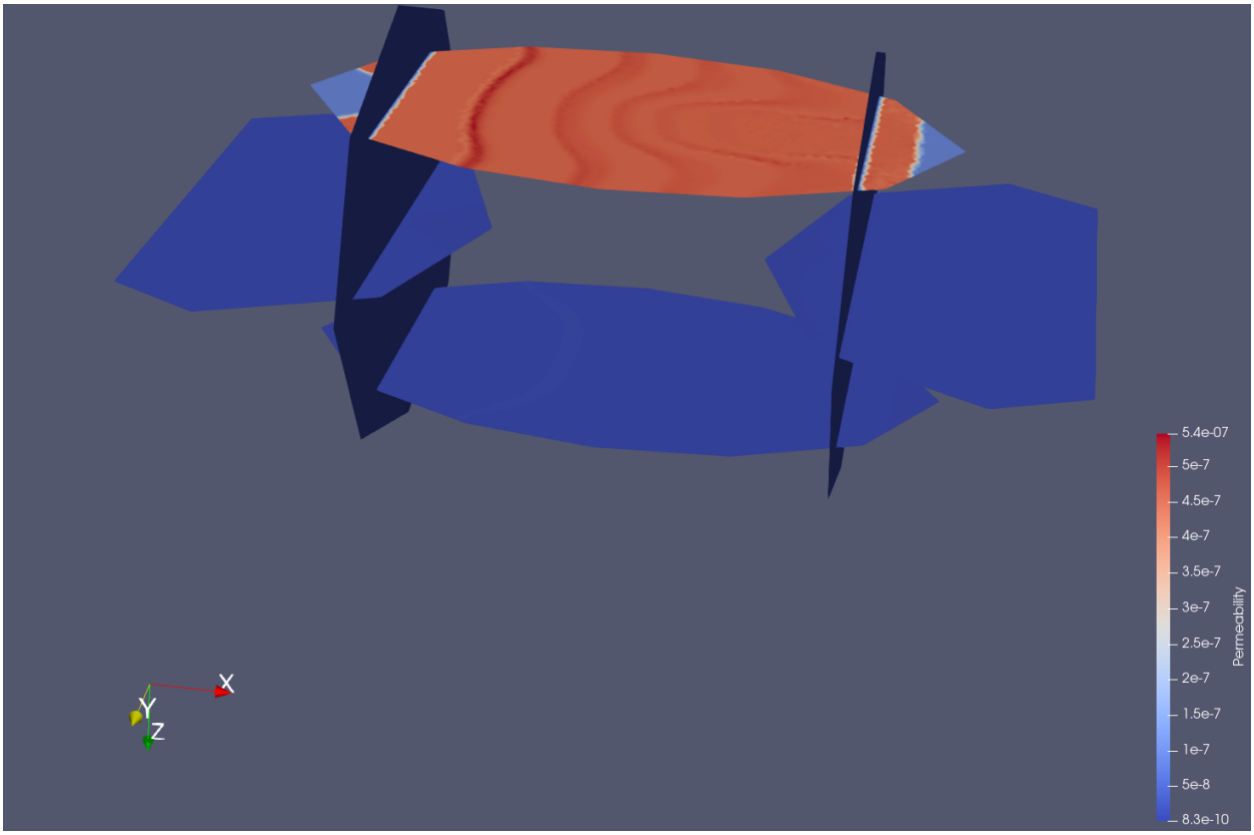

Figure 10. Chemistry model for discrete fracture networks (permeability at time = 100 days)

Chapter 6

Conclusions and Recommendations

This thesis demonstrates the utility of discrete fracture network modeling for simulating mineral precipitation in fractures under geologic reservoir conditions. Mineral precipitation is an important, but relatively understudied, process that can occur via natural processes like mineral weathering, or through injection or extraction of fluids in underground reservoirs. Understanding relationships among mineral precipitation and fracture permeability is critical in low-permeability reservoirs, where the matrix porosity and connectivity are low and fluid transport primarily occurs in fractures. Modeling the onset and distribution of precipitates through fracture networks (in this thesis, using dfnWorks) can improve our understanding of when and where these reactions occur and identify behavior that may be missed in more simplistic models that do not explicitly resolve the fractures themselves.

Beyond the direct contributions of this thesis, in presenting the status quo and recent advancements in modeling reactive transport in fractures and developing the initial code to simulate precipitation in fractures using dfnWorks, this thesis also lays the groundwork for future studies to understand how precipitation affects fracture permeability in various situations. Future research should continue to build upon the initial code presented herein to simulate dissolution-precipitation and resultant permeability changes over different scenarios of interest, such as varying initial fracture networks and mineral content (alongside associated reaction rates). Ultimately, this process could be used to develop permeability relationships resulting from dissolution-precipitation in various rock types and/or fracture networks and can improve our ability to anticipate when precipitation will either reduce permeability or proceed in a way that

leaves permeability intact. The latter is important to a host of energy technologies where precipitation due to fluid-rock interactions can occur and either be detrimental or neutral to permeability, including mineral scale formation in unconventional oil/gas production or geothermal reservoirs and mineral trapping during geologic CO_2 storage.

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