MULTISCALE CHEMO-MECHANICAL COUPLING EFFECTS FOR POROUS MEDIA

# Multi-scale chemo-mechanical coupling effects for fluid-infiltrating porous media: theory, implementation, and validation

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A Thesis Submitted to the School of Graduate Studies in the Partial Fulfillment of the Requirements for the Degree of

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# Lay Abstract

This thesis presents the comprehensive behaviors of geomaterials under mechanical, fluid, and chemical interactions, which result in displacement and cracking. Since there is no existing software or simulation tool that includes all the physical behaviors considered in this dissertation, the development and implementation of these physical mechanisms, followed by testing and analysis for engineering problems, constitutes the main contribution of this work. The newly developed simulation tool ranges from simulating the mechanical behavior of porous media saturated with water and reactive fluid to modeling the seepage of water/reactive fluid that triggers damage (cracks) in the porous media. This simulation tool can effectively analyze engineering problems that focus on the interactions between the working fluid and the host solid matrix under complex solution conditions. Examples include modeling carbon sequestration in saline aquifers and the storage of nuclear waste in subsurface repositories etc. The simulation tool proposed in this thesis incorporates rigorous mathematical derivations, efficient and accurate multiscale discretization techniques, robust non-iterative and iterative numerical coupling strategies, and thorough comparisons between numerical results and experimental/laboratory data. Simultaneously, it is important to recognize the model's limitations. Although the model assumes local equilibrium and interactions between physical mechanisms, it cannot fully capture all behaviors under these assumptions due to the restrictions in our understanding and potential constraints of numerical methods.

# Abstract

As climate change escalates and the demands for energy resources increase, modern geotechnical engineering must tackle critical challenges to ensure sustainable development and enhance the resilience of infrastructure in society. The coupled chemo-hydromechanical processes in multiphase materials present significant challenges in geotechnical engineering, particularly for applications like carbon sequestration, geological disposal of nuclear waste, and hydraulic fracturing with reactive fluids, all of which involve highly heterogeneous and strongly anisotropic multiphysics environments. This dissertation introduces a multiphysical computational framework specifically designed to address the challenges associated with these unconventional applications.

In this dissertation, we consider not only the local multiphysical coupling effects in the constitutive model but also the nonlocal effects arising from pore fluid flow, chemical species convection and diffusion, chemical reactions occurring in both solid and fluid constituents, and damage due to fluid pressure acting on fractures in the solid. We have integrated all these physical processes and developed a single unified model capable of handling the complex hydro-chemo-mechanical responses of geomaterials under varying geochemical conditions, confining pressures, and external loading scenarios. This computational framework offers a comprehensive simulation tool to investigate the long-term stability of geomaterials, which is determined by the intensity of chemical reactions under specific temperature and pressure conditions (assuming an isothermal condition in this dissertation), as well as the sustainability of geotechnical infrastructure in erosive environments driven by both mechanical and chemical processes.

Three key aspects of engineering applications related to the effects of chemical reactions in geotechnical engineering are addressed. Firstly, we have integrated a complete calcite reaction system into poromechanics to couple pore geochemistry with poroelasticity theory. This integration is capable of predicting the geomechanical response essential for long-term stability analysis in  $CO_2$  sequestration engineering. Key features of this model include a multi-field finite element approach, local-equilibrium explicit geochemistry characterization of the calcite dissolution/precipitation reaction system, a robust algorithm for sequentially coupling pore geochemistry with poromechanics, and strategies to enhance the computational efficiency of solvers. Secondly, for applications involving acid working fluids in hydraulic fracturing, we have extended and adapted previous models within the phase field method framework. This extended integration effectively addresses the effects of chemically assisted fracturing in hydraulic fracturing

operations. The key innovations of this model are the implementation of the phase field method to capture crack behaviors with poromechanics, the modeling of acid fluid transport in porous media and fractures, and its application to multiple mineral reaction systems. Thirdly, we have proposed a constitutive model that incorporates pore geochemistry and the pressure dissolution effect into internal variables, effectively capturing the chemical reactions contributing to softening in geomaterials. This model effectively illustrates and predicts chemically induced weathering or damage in granular porous media, such as sinkholes and subsidence. Derivations of a thermodynamicallybased degradation index consider the influences of pore geochemistry and contact forces between grains and bonds. The model also proposes cross-scale relationships that consider reaction effects from individual particle sizes to particle aggregates. Furthermore, these relationships are incorporated into classical Cam-Clay-type models, along with the derivation of a consistent tangent modulus.

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## **Declaration of Academic Achievement**

I, Yongfan Guo, declare that this thesis titled, Multi-scale chemo-mechanical coupling effects for fluid-infiltrating porous media: theory, implementation, and validation, and works presented in it are my own. I confirm that the bibliographical details of the work are outlined below:

- Guo, Y. (80 %), Na, S. H. (20 %). A computational framework based on explicit local chemical equilibrium for coupled chemo-hydro-mechanical effects on fluidinfiltrating porous media[J]. Journal of Computational Physics, 2023, 488: 112196. (Appeared in Chapter 2)
- Guo, Y. (80 %), Na, S. H. (20 %). A reactive-transport phase-field modelling approach of chemo-assisted cracking in saturated sandstone[J]. Computer Methods in Applied Mechanics and Engineering, 2024, 419: 116645. (Appeared in Chapter 3)
- Guo, Y. (75 %), Na, S. H. (20 %), Guo, P. (5 %). Thermodynamical Constitutive Modeling on Chemically-Induced Degradation of Grain and Bond in Cohesive Granular Materials. (To be submitted to Computers and Geotechnics) (Appeared in Chapter 4)

Student signature:

Date:

We, Peijun Guo and SeonHong Na certify that the student's statements regarding their contribution to each of the works listed above are correct.

Coordinating supervisor signature:

Date:

## Chapter 1

# Introduction

## 1.1 General background and literature review

The key research point of this dissertation is the investigation of the influence of the chemical reactions that occur in fluid flow on the mechanical response of the geomaterials. However, reaching the point is not as simple as a description in one sentence. We compress as many necessary details as possible into as few words in the title of the dissertation. Nonetheless, a general background and literature review are indispensable for readers to learn more about the background and the research needed for this work to contribute to developing the subfield community. Therefore, this section presents a general background and puts the research needs of this work within different subfields to review the current research progress and identify existing gaps.

We know that numerous applications in geotechnical engineering involve multiscale and multiphysics processes. By unpacking the terminologies *multiphysics* and *multiscale* in the context of engineering applications, we can get deeper insights into the research purposes and goals within this subfield. *Multiphysics* typically implies that at least two or more physical fields are coupled within a problem. The most comprehensive and complex problem in geotechnical engineering is the thermo-hydro-mechanical-chemicalbio-electrical coupling problem. However, these problems can be simplified for different applications into fewer coupled fields (Yin et al., 2023). For example, internal erosion, hydraulic fracturing, heat transfer energy piles, municipal waste disposal, production from unconventional oil and gas reservoirs, heat stimulation and depressurization of natural gas hydrate formations, pavements subjected to heating-cooling cycles, contaminant transport, and CO<sub>2</sub> sequestration are related to two, three, or even four coupled physical fields. These include hydro-mechanical, thermal-mechanical, chemo-mechanical, hydro-thermal-mechanical, and thermal-hydro-chemical-mechanical problems. *Multiscale*  typically implies that a problem in an application spans an immense range of spatial and temporal scales. The spatial scale of interest can range from the nanoscale to the microscale, mesoscale, and even to hundreds of kilometers. The timescale of interest can range from nanoseconds to several hundreds or even thousands of years. Thanks to significant advancements in testing methods, equipment design, and computing power available to modern geotechnical engineering, these complex coupling problems are being solved step by step through multiscale laboratory testing and numerical simulations. This dissertation focuses on coupled problems involving the chemical reactions of solid minerals and the mechanical response at multiple scales. We introduce the research needs from four key perspectives.

## 1.1.1 Multiscale and multiphase modeling of flow in porous media coupled with geomechanics

The primary interest of this work is the coupling of fluid flow and soil mechanics. We investigated research from the past ten years, with a particular focus on multiscale modeling and the simulation of multiphase flow in porous media coupled with geomechanics. The scope of the literature review in this section focuses on physical-based algorithms for modeling and simulation of flow and transport in geomechanics and complex hydrological formations. Problems highly relevant to complex chemical conditions in engineering applications, such as  $CO_2$  sequestration in saline aquifers,  $CO_2$  enhanced oil recovery, and the storage of nuclear waste in subsurface repositories, were selected. Table 1.1 summarizes the research addressing *Multiscale Modeling and Simulation of Multiphase Flow in Porous Media Coupled with Geomechanics* from September 2004 to June 2018 (Wheeler et al., 2019).

Their systematic work on this topic addresses most of the key questions about the coupling between fluid flow and geomechanical environments, particularly regarding the implementation of numerical algorithms. Using the Finite Element Method, the most representative work focuses on fluid flow, the constitutive model of the solid phase, and the coupling of fluid-solid mechanics. The fluid flow problems involving local conservation, flux approximation, flux-continuous velocity, and multiple boundary conditions are crucial elements that were carefully considered (Ganis et al., 2015; Singh and Wheeler, 2016). Moreover, the compositional model used in multiphase fluid, including the equilibrium and kinematic conditions imposed on the interface between solid and fluid, lays a solid foundation for mineral dissolution problems in our model (Ganis et al., 2019; Ambartsumyan et al., 2019). When solving the strongly coupled problems between pore pressure and solid displacement, it was necessary to adopt a block preconditioner

and assemble the global Jacobian to ensure stabilization under conditions of very low permeability (Ganis et al., 2014a,b).

Literature	Algorithm Approach	Novel point	Notes
Ganis et al. (2014a)	mortar mixed finite element method	linearize subdomain & form global Jacobian	multiscale & flow model
Ganis et al. (2014b)	mortar mixed finite element method	Schur complements & two-stage preconditioner	multiscale & flow model
Ganis et al. (2015)	multipoint flux mixed finite element method	flux-continuous velocity approximation	single phase & flow model
Ganis et al. (2019)	enhanced velocity mixed finite element method	allow dynamic adaptive mesh refinement	multiphase compositional & flow model
Khattatov and Yotov (2019)	multiscale mortar mixed finite element method	realize linear elasticity with weakly enforced stress symmetry	multiscale & solid model
Kumar et al. (2016)	undrained split iterative method	flow step is different from mechanics step	coupled flow and geomechanics
Singh and Wheeler (2016)	multi-point flux mixed finite element method	local mass conservation, multiple boundary conditions & accurate flux approximation	complex compositional model & flow model

TABLE 1.1: Summary of literature on numerical algorithm approaches for multiscale and multiphase flow in geomechanics

TABLE 1.1: Summary of literature on numerical algorithm approaches for multiscale and multiphase flow coupled in geomechanics (continued)

Literature	Algorithm Approach	Novel point	Notes
Ambartsumyan et al. (2019)	semidiscrete continuous-in-time finite element method	equilibrium and kinematic conditions are imposed on the interface	quasi-Newtonian free fluid coupled with the poroelasticity

This dissertation begins with the stabilized finite element methods for coupled flow and geomechanics. To lay the foundation for the discussion in Chapters 2 to 4, we introduce the simplest basic problem and connect it to the following literature review. The rudimentary case for the coupled problem requires (White, 2009),

$$\nabla \cdot \boldsymbol{\sigma}' - \nabla p + \rho \boldsymbol{g} = 0; \tag{1.1}$$

$$\nabla \cdot \dot{\boldsymbol{u}} + \nabla \cdot \tilde{\boldsymbol{v}} = 0; \tag{1.2}$$

where the first equation is a momentum balance equation, relating the effective stress  $\sigma'$ in the solid matrix, the pore water pressure p, and a body force due to the mixture of density, with the second equation representing the mass balance equation that imposes a solution on the displacement  $\dot{u}$ , and the seepage velocities  $\tilde{v}$ . Two additional constitutive relationships are included in the system. The first, widely accepted by the porous media research community, relates seepage velocity to the pore pressure gradient, a relationship known as the generalized Darcy's law (Darcy, 1856):

$$\tilde{\boldsymbol{v}} = -\frac{\boldsymbol{k}}{\nu} (\nabla p - \rho_f \boldsymbol{g}); \qquad (1.3)$$

where we have introduced the permeability of porous media k, dynamic fluid viscosity  $\nu$ , and the fluid density  $\rho_f$ .

The second equation connects the displacement u to the effective stress  $\sigma'$ . Under the small strain assumption, it can be expressed using tensor calculus, which is commonly

employed in continuum mechanics,

$$\boldsymbol{\sigma}' = \mathbb{C} : \boldsymbol{\epsilon}; \ \boldsymbol{\epsilon} = \frac{\nabla \boldsymbol{u} + \nabla \boldsymbol{u}^T}{2}$$
(1.4)

where  $\boldsymbol{\epsilon}$  is the strain tensor, and  $\nabla \boldsymbol{u}$  and  $\nabla \boldsymbol{u}^T$  represent the displacement gradient and the transpose of the displacement gradient, respectively. The term  $\frac{\nabla \boldsymbol{u} + \nabla \boldsymbol{u}^T}{2}$  is referred to as the infinitesimal strain tensor.  $\mathbb{C}$  is a fourth-order tensor representing tangential moduli, and the symbol ':' denotes a double contraction.

The equations governing the linear momentum and mass balance can be solved both accurately and efficiently using a robust Mixed Finite Element Method, implemented with the open-source finite element library deal.II (https://dealii.org). However, these are still far from sufficient for our problem. To better characterize the reactive flow in saturated geomechanics, we must go through three important steps to transition from a mathematical framework to a working model.

- We need to incorporate reaction details and introduce them into Eq. 1.2. These models must reflect the conservation law for mass balance and be both accurate and efficient.
- There should be a constitutive modeling effort. This aspect focuses on Eq. 1.3 and Eq. 1.4.
- It is necessary to consider the damage, not only the deformation, of the porous media. This means Eq. 1.1 should be revised or extended to incorporate the influence of damage.

Next, we review the contributions of the research community and identify the research needs for this dissertation on these three aspects.

#### 1.1.2 Chemo-mechanical coupling effects on geomaterials

The most important task regarding chemo-mechanical coupling effects in this dissertation is the introduction of reactive transport modeling to study geochemically driven processes and alterations in porous media. Reactive transport modeling employs key-process-based models that predict the transport of reactive solutes in both fractured and intact porous media. These models account for structural changes in porous media coupled with (bio-)chemical and hydraulic processes, as well as thermal and mechanical processes (Steefel et al., 2015; Deng et al., 2021a, 2022). As mentioned in Section 1.1.1, multiscale and multiphysical characteristics are particularly distinct in problems involving geochemical reactions. This is because different chemical-physical processes have distinct characteristic time and length scales. For example, Figure 1.1 illustrates a sequence that reflects a certain (bio)chemical process from the micro- to the macro-scale. This sequence encompasses a broad scope for upscaling specific microscopic mechanisms to the desired scale. The transition between the different scales presents numerous challenges.

Recent research progress has mainly focused on the pore scale/pore network models, micro-continuum scale, and continuum scale that nearly covers the entire sequence of upscaling shown in Figure 1.1. We now review the main contributions in this field, focus on our specific approaches, and present the basic ideas that this dissertation contributes to the topic of chemo-mechanical coupling in geotechnical engineering. Advanced



FIGURE 1.1: The general upscaling sequence from pore-scale to fieldscale. Characteristics of the medium are determined at different scales, either alone or in combination. (modified by Deng et al. (2022) after Hajizadeh et al. (2011); Blunt et al. (2013))

characterization techniques for pore space allow the intrinsic spatial heterogeneity of porous media to more closely resemble real-world conditions (Blunt et al., 2013; Sadeghnejad et al., 2021). These techniques provide extensive information about the geometry, topology, and mineralogy necessary for simulating physical and geochemical processes (Dupin et al., 2001; Thullner and Baveye, 2008; Jamshidi et al., 2009; Raoof and Hassanizadeh, 2010; Lopez-Peña et al., 2019). Currently, computational algorithms have been developed from various aspects. Calculations at the pore scale employ computational fluid dynamics methods, such as the level set method (Prodanovic et al., 2010; Jettestuen et al., 2013), volume of fluid methods (Raeini, 2013; Shams, 2018; Li et al., 2022; Molins et al., 2021), particle tracking approaches like the Lattice Boltzmann method (Chen et al., 2018; Zuo et al., 2023), and smoothed particle hydrodynamics (Yang et al., 2020; Zhu and Fox, 2002). The pore network models connect individual pores through throats with idealized geometries, facilitating a focused investigation of the complex structure of the porous medium. Flow or reactive solute transport problems can be solved using predefined distributions of pore and throat lengths and diameters (Vogel et al., 2010). However, pore-scale applications in deforming porous media have been limited in study until now. On the one hand, the complexity of pore-scale or pore network models is computationally demanding and requires significant computational resources. Additionally, the transport behaviors of fluids at this scale are still not fully understood. Simple applications of mechanical changes in porous media, including dissolution and precipitation reactions, can lead to particle displacement and migration (Noiriel, 2015). Pore-scale deformation can affect changes in porosity and permeability (Yoon et al., 2012; Kang et al., 2014; Spokas et al., 2019). Some pore network models have also accounted for relatively complex fluid behaviors, enabling the calculation of sorption between the solid matrix of the porous medium and the adsorbed fluid by considering both the elastic energy stored in the medium and the energy interactions between the adsorbates (Bakhshian and Sahimi, 2017).

Pore-scale models have distinct features for characterizing the solid-fluid interface, making them highly predictive for coupled chemical-physical processes, especially at the interfaces. However, this also represents a significant limitation of these models due to the high demand for computational resources and the very limited computational domain. Typically, such a domain is constrained to around 1 cm in dimensions because of the limitations in accurately describing the pore network using scanning techniques. Hybrid and micro-continuum models have become popular in recent years as multiscale strategies to upscale key information obtained from finer-scale modeling. We collected and reviewed several models for hybrid modeling, particularly addressing the boundaries between subdomains, as detailed in Table 1.1. In the micro-continuum method, the specific or bulk surface area is characterized at the continuum scale, with the porous media distinguished by its local porosity. The governing equations are solved across the entire computational domain. As illustrated in the conceptual diagram of the micro-continuum scale model (Figure 1.2), micro-continuum scale reactive transport models serve as a valuable tool for investigating and quantifying how small-scale chemical (e.g., mineral composition) and physical heterogeneities (e.g., micro-porosity) influence solute transport



and system evolution in larger domains (Deng et al., 2022). Representative works study

FIGURE 1.2: Examples of interface representation and evolution for dissolution or precipitation processes are as follows: (a) Interface representation in the physical domain is shown by a solid line, with its evolution depicted by a dotted line; n is the vector normal to the surface. (b) Micro-continuum representation of the interface in control volumes (filtering approach) is illustrated, where each control volume has a porosity ranging from the internal porosity of the solid (dark blue) to 1 (light blue, fluid phase). Selected from Noiriel and Soulaine (2021).

the preferential flow and mineral dissolution of porous media or fractured porous media, describing the boundary evolution that leads to the formation of channels and wormholes. For example, Ormond and Ortoleva (2000) conducted a comparative study to illustrate the differences in the shape and temporal evolution of wormholes using a continuum approach versus a micro-continuum approach. Another important application of the micro-continuum reactive transport model is the study of surface evolution during the precipitation process. Several research works have reported on the crystallographic orientations and growth on the solid-fluid interface (Yang et al., 2021), homogeneous nucleation in the solution, and upscaling in continuum-scale problems (Noiriel et al., 2012; Rajyaguru et al., 2019; Deng et al., 2021b).

Finally, we introduce the continuum-scale models, which form the main scale of discussion for this dissertation. We also highlight the conceptual illustration of the key ideas for this work. The continuum-scale model is the most general approach, widely used in specimen, field, and even kilometer-scale simulations. The basic idea of the continuum-scale model is averaging over the representative elementary volume (REV) that incorporates micro-scale information about pore sizes, mineral grain sizes, and mineral compositions into a continuum scale (mm scale or m scale) REV (Bear, 2013). The effective constitutive parameters for continuum-scale models provided by micro-scale studies include permeability, porosity, tortuosity, dispersivity, reaction rate, the chemical

equilibrium constant, mineral compositions, etc. (Lichtner and Kang, 2007). We note that the constitutive parameters in classical models are sometimes derived from justified or historically matched values. However, in this dissertation, we prefer to select the upscaling approach from the micro-scale to obtain the constitutive parameters. This approach allows us to consider more microscale phenomena and incorporate them into the macro-scale behaviors of solid geomaterials. In this dissertation, as shown in Figure



FIGURE 1.3: A schematic description of various multiphysics at the multiscale level. (Collect and revised from Noiriel and Soulaine (2021); Guo and Na (2023, 2024))

1.3, we examine the governing laws derived from microscopic observations, particularly focusing on the chemical reactions between multiple components. We then connect these chemical components to solid reactions to investigate further the morphologic influences on solids, which may induce changes in hydraulic and mechanical properties. Subsequently, we assess the impacts on single-grain bodies and scale up to grain-sized aggregates, ultimately performing calculations at the continuum level.

### 1.1.3 Phase field approach for multiphysical problems

Phase field models have received increasing attention in recent years because they can elegantly simulate complex fracture processes, including the fracture behavior under multiphysics conditions. Here, we briefly introduce the research progress and theoretical developments on phase field models for fracture and their coupling with the finite element method. We will also mention the established modules in the mainstream code and outline the general implementation approach for this dissertation.

Based on the comprehensive review by Zhuang et al. (2022) on the phase field method and its computer implementation, phase field models serve different purposes in the physical and mechanical communities. In the physics community, Landau-Ginzburg phase transition theory models typically describe phase changes without incorporating a length scale, where the order parameter smoothly transitions between phases. The free energy in the physical community does not include the fracture energy. Some representative works have established milestones in developing the phase field method within the physical community. Aranson et al. (2000) was the first to propose phase field-like descriptions of crack propagation in brittle materials. Their model focuses on Mode-I Fracture (Opening Mode Fracture) and simulates the atomic bond-breaking process. Karma et al. (2001) proposed a phase field model for Mode-III Fracture (Tearing Mode Fracture). Their model maintained thermodynamic consistency to ensure energy conservation. Consequently, the energy functional governed the main system equations, including the momentum balance equation, the stress-strain relationship, and the phase-field evolution equation. Henry and Levine (2004) presented a model that effectively simulated crack growth for Mode-I Fracture (Opening Mode Fracture) and Mode-II Fracture (Sliding Mode Fracture) under 2D plane strain conditions. Compared to the work of Karma et al. (2001), their model can effectively handle more complex physical processes while maintaining thermodynamic consistency. For example, it couples the phase field with the elasticity field to optimize the response between stress and strain. Overall, phase field models in the physics community focus more on the thermodynamic and kinetic studies of the microstructure of materials, such as phase transition, phase separation, thermodynamics, kinetics, and microstructure simulation.

In the mechanical community, phase field models are based on Griffith's fracture theory. The early phase field model, developed for quasi-static fractures, was established by Miehe et al. (2010a). This approach, known as the variational approach for brittle fracture, was introduced by Francfort and Marigo (1998). The regularization formulation was derived by Bourdin et al. (2000). Kuhn and Müller (2008) further developed the model by decomposing the elastic energy and releasing energy for cracking. The description of energy is quite similar to that of Karma et al. (2001), but it is better suited for dealing with mixed fracture modes (Mode I/II/III) under complex stress states. In the early phase-field simulations in the mechanical community, researchers did not distinguish strain into

compression and tension components. As a result, unrealistic crack patterns, such as those caused by compression, were reported by Bourdin et al. (2000). Amor et al. (2009) further advanced the elastic energy decomposition by separating it into volumetric and deviatoric components. Crack evolution is then driven only by the positive components of the elastic energy. In other words, only volumetric dilation and shear deformation contribute to crack formation. Miehe et al. (2010a,b) developed a thermodynamically consistent phase field model of brittle fracture. They also distinguished the energy decomposition, but followed the compression and tensile parts of the energy, and introduced a degradation of the compressive energy component, whereas Amor et al. (2009) only considered the deviatoric stress. Another important feature of the model is the use of an irreversible historical field to ensure a monotonically increasing phase field, which facilitates the realization of computer implementation. Regarding multiphysics problems, we follow the summary by Zhuang et al. (2022) to list the main forms of the governing equations for the phase field model. This dissertation builds on that framework to further explore the complex interactions between the phase field and other physical fields. This introduction lays a mathematical background for the details in Chapter 3.

Formulation type	Governing equations	Historical field
Isotropic	$\begin{cases} \nabla \cdot \boldsymbol{\sigma} + \boldsymbol{b} = 0 \\ -l_0^2 \Delta \phi + \phi = \frac{2l_0}{G_c} (1 - \phi) H \\ \boldsymbol{\sigma}(\boldsymbol{u}, \phi) = (1 - \phi)^2 \frac{\partial \Psi_0}{\partial \boldsymbol{\epsilon}} \\ \mathbb{C} = \frac{\partial \boldsymbol{\sigma}}{\partial \boldsymbol{\epsilon}} \end{cases}$	with energy decomposition of volumetric and deviatoric
Anisotropic (Miehe et al., 2010a)	$\begin{cases} \nabla \cdot \boldsymbol{\sigma} + \boldsymbol{b} = 0\\ (\frac{2l_0H}{G_c} + 1)\phi - l_0^2 \nabla^2 \phi = \frac{2l_0}{G_c}H\\ \boldsymbol{\sigma}(\boldsymbol{u}, \phi) = (1 - \phi)^2 \frac{\partial \Psi_{\epsilon}^+}{\partial \epsilon} + \frac{\partial \Psi_{\epsilon}^-}{\partial \epsilon}\\ \mathbb{C} = \frac{\partial \boldsymbol{\sigma}^+}{\partial \epsilon} + \frac{\partial \boldsymbol{\sigma}^-}{\partial \epsilon} \end{cases}$	with energy decomposition of compression and tension, and degrade the compression

TABLE 1.2: Summary of formulations of the phase field models in mechanics community (revised from Zhuang et al. (2022))

 TABLE 1.2: Summary of formulations of the phase field models in

 mechanics community (continued)

\_\_\_\_\_

Formulation type	Governing equations	Historical field
Anisotropic (Amor et al., 2009)	$\begin{cases} \nabla \cdot \boldsymbol{\sigma} + \boldsymbol{b} = 0 \\ - l_0^2 \Delta \phi + \phi = \frac{2l_0}{G_c} (1 - \phi) H \\ \boldsymbol{\sigma}(\boldsymbol{u}, \phi) = (1 - \phi)^2 \frac{\partial \Psi_{\epsilon}^+}{\partial \epsilon} + \frac{\partial \Psi_{\epsilon}^-}{\partial \epsilon} \\ \mathbb{C} = \frac{\partial \boldsymbol{\sigma}^+}{\partial \epsilon} + \frac{\partial \boldsymbol{\sigma}^-}{\partial \epsilon} \end{cases}$	with energy decomposition of compression and tension, and contribution of deviatoric
Hybrid (Ambati et al., 2015)	$\begin{cases} \nabla \cdot \boldsymbol{\sigma} + \boldsymbol{b} = 0 \\ -l_0^2 \Delta \phi + \phi = \frac{2l_0}{G_c} (1 - \phi) H \\ \boldsymbol{\sigma}(\boldsymbol{u}, \phi) = (1 - \phi)^2 \frac{\partial \Psi_0}{\partial \boldsymbol{\epsilon}} \\ \mathbb{C} = \frac{\partial \boldsymbol{\sigma}}{\partial \boldsymbol{\epsilon}} \end{cases}$	with energy decomposition of compression and tension, but only taking of compression
Hybrid (Zhang et al., 2017)	$\begin{cases} \nabla \cdot \boldsymbol{\sigma} + \boldsymbol{b} = 0\\ (1 - \phi)(\frac{H_1}{G_{cI}} + \frac{H_2}{G_{cII}}) - \frac{1}{2l_0}\phi + \frac{l_0}{2}\delta\phi = 0\\ \boldsymbol{\sigma}(\boldsymbol{u}, \phi) = (1 - \phi)^2 \frac{\partial \Psi_0}{\partial \boldsymbol{\epsilon}}\\ \mathbb{C} = \frac{\partial \boldsymbol{\sigma}}{\partial \boldsymbol{\epsilon}} \end{cases}$	with energy decomposition of compression, and critical energy release rate of Mode I & II
Hybrid (Zhou et al., 2019)	$\begin{cases} \nabla \cdot \boldsymbol{\sigma} + \boldsymbol{b} = 0 \\ -l_0^2 \Delta \phi + \phi = \frac{2l_0}{G_c} (1 - \phi) H \\ \boldsymbol{\sigma}(\boldsymbol{u}, \phi) = (1 - \phi)^2 \frac{\partial \Psi_0}{\partial \boldsymbol{\epsilon}} \\ \mathbb{C} = \frac{\partial \boldsymbol{\sigma}}{\partial \boldsymbol{\epsilon}} \end{cases}$	with consideration of compression- shear effects for fracture

The governing equations in Table 1.2 show that the displacement  $\boldsymbol{u}$  is coupled with the phase-field parameter  $\phi$ . The main formulation types developed recently are isotropic, anisotropic, and hybrid approaches. The corresponding historical fields for the fracture driving forces are included in the table. The core difference in these governing equations lies in how they handle energy decompositions. In our work, we integrate interactions of mechanisms from multiple physical fields and consider the energy contribution of each field. We further derive a new historical field for driving forces for cracking. Another significant contribution of this dissertation is implementing the finite element method to solve the governing equations and realize the complex coupling relationships between different mechanisms. Therefore, we will further review the progress in these areas.

Various numerical discretization approaches can be coupled with the phase field method. The representative methods include the isogeometric method (Borden et al., 2014; Schillinger et al., 2015; Ambati and De Lorenzis, 2016; Goswami et al., 2020b), meshfree method (Amiri et al., 2016), physics-informed neural networks (Goswami et al., 2020a), and the FFT algorithm (Chen et al., 2019). The finite element method is the most common approach to solving the phase field evolution equations. Many applications and algorithmic research efforts have employed the finite element method to solve phase field equations, especially for basic analyses of multiphysical problems (Kuhn and Müller, 2008; Amor et al., 2009; Miehe et al., 2010a,b; Bourdin et al., 2012; Wheeler et al., 2019; Lee et al., 2017; Schuler et al., 2020; Zhou et al., 2018, 2019; Guo and Na, 2024). A detailed finite element approximation is provided in Chapter 3, so we will not elaborate on it here. In the remainder of this section, we will introduce this dissertation's solution schemes and coupling concepts. The common approaches to solving the discretized equations in numerical simulations are monolithic and staggered schemes. In some research, displacement and the phase field are solved simultaneously (Liu et al., 2016), while in other works, the phase field and displacement are solved independently using a staggered scheme (Seleš et al., 2019). Generally speaking, these two approaches are similar under certain conditions, but numerical simulation efficiency differs between them. This dissertation considers both monolithic and staggered schemes, taking into account the coupling relationships between different physical fields to determine the appropriate scheme. As shown in Figure 1.4, in the solid mechanics module, the principal strain and principal direction can be obtained from the spectral decomposition method. These decomposed parts can be transferred into the phase field to solve the historical strain and further derive the necessary information to solve the phase field evolution equation, such as the crack driving force and energy release rate. The phase-field parameter represents the degradation of the solid material and is integrated into the consistent tangent operator



FIGURE 1.4: Established coupling and modulus relations for phase-field modeling (referred to Zhuang et al. (2022))

to capture damage evolution. This parameter modifies the stress-strain relationship at finite element integration points, ensuring accurate and stable convergence of the numerical solution, while also capturing the material's progressive stiffness reduction leading to crack nucleation.

#### 1.1.4 Constitutive models on chemo-mechanical effects for porous media

Finally, we discuss the research progress on constitutive modeling of chemo-mechanics in porous media. As discussed in the previous review, when the solid skeletons of geomaterials dissolve, their strength weakens, and their stiffness softens. Variations in mineralogical compositions undermine the stability and sustainability of geotechnical and geological systems during dissolution. However, previous studies have primarily focused on the coupling of multiphysical mechanisms, without adequately capturing the material's softening effects. In the following sections, this dissertation reviews research approaches to explore the impact of chemical reactions on mechanical constitutive features.

The general approach based on classical constitutive models has been developed over several decades. A successive Cam-Clay-type model was extended by incorporating an internal variable to control plastic hardening and approximate the effects of chemical dissolution on mechanical properties (Nova et al., 2003; Buscarnera, 2012; Buscarnera and Das, 2016). Additionally, some researchers have proposed to examine the material properties at different scales and connect them to the measurement of the weathering or degradation of the material (Hueckel et al., 2016; Ciantia and Hueckel, 2013). A further development of these models is the analysis of the stiffness degradation of calcarenite samples both before and after the elastic limit (Gajo et al., 2015, 2019; Ciantia, 2018). This kind of model has the advantage of considering the intrinsic connections between microscopic and macroscopic scales to reproduce the mechanical response close to the complex external loading conditions. However, when considering the complex chemical reactions that take place, the elastoplastic model lacks a rigorous thermodynamic foundation, and the evolution of internal variables is not always accurately captured. Some constitutive models based on thermodynamics (described in strain or stress space) provide alternative approaches to modeling soil behavior under strict thermodynamic restrictions. Representative efforts include developing hyperelasticity with pressure-dependent elastic stiffness and plasticity based on various thermodynamic frameworks. For example, Zhang and Cheng (2014, 2015) proposed a model to consider the granular thermodynamics which has the potential to model the thermo-mechanical coupling in soil mechanics (Zhang, 2017), anisotropic hyperelasticity for granular soils (Xiao et al., 2020), and granular fabric evolution (Zhang and Soga, 2021).

Literature years	Multiphysics							
	Η	$\mathbf{M}$	$\mathbf{C}$	$\mathbf{T}$	$\mathbf{E}$	Р	D	Ca
1993~1996		$\checkmark$	$\checkmark$					
2003~2010		$\checkmark$	$\checkmark$					
2002 ~2004		$\checkmark$	$\checkmark$			$\checkmark$		
2011~2013		$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$		
2012~2021		$\checkmark$	$\checkmark$	$\checkmark$				
$2012 \sim 2018$		$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$			
1959		$\checkmark$						$\checkmark$
2001~2002		$\checkmark$				$\checkmark$		$\checkmark$
2011~2018		$\checkmark$	$\checkmark$					$\checkmark$
$2013 \sim 2018$		$\checkmark$	$\checkmark$	$\checkmark$				$\checkmark$
2016		$\checkmark$	$\checkmark$	$\checkmark$		$\checkmark$		$\checkmark$

TABLE 1.3: An overview of thermodynamically consistent THCM constitutive theories for geo-energy applications (revised from Siddiqui et al. (2024))

Literature years Multiphysics  $\mathbf{T}$ Η  $\mathbf{M}$  $\mathbf{C}$  $\mathbf{E}$  $\mathbf{P}$ D Ca  $\checkmark$ 2022  $\checkmark$  $\checkmark$  $\checkmark$  $\checkmark$ 

TABLE 1.3: An overview of thermodynamically consistent THCM constitutive theories for geo-energy applications (continued)

Note: H: Hydraulic; M: Mechanical; C: Chemical; T: Thermal; E: Electrical; P: Plasticity; D: Damage; Ca: Capillarity.

Building upon the initial overview provided by Siddiqui et al. (2024), we summarize and list in Table 1.3 the substantial improvements made over the years to thermodynamicallybased constitutive models developed for subsurface geomaterials in geo-energy applications. This table highlights the significant advancements of these models, with more progress anticipated. From a thermodynamic viewpoint, multiphysics can be integrated into constitutive laws. Although THCM (Thermo-Hydro-Chemo-Mechanical) constitutive modeling has received significant attention, there remains a lack of focus on incorporating additional physics such as damage, plasticity, electrical effects, and unsaturated (capillary) conditions into a comprehensive multiphysics framework. In this case, our previous work with a comprehensive computational framework that addresses hydro-chemo-mechanicaldamage coupling allows us to demonstrate the thermodynamic framework's capability to provide detailed insights into granular cohesive porous media, enabling us to extend the classical constitutive model to encompass additional multiphysics considerations.

## **1.2** Summary of contributions

This section provides a summary of the key contributions of this dissertation. The topic of this work is the computational modeling of the chemo-mechanical effects in geological material. Among the multiple complex coupling effects of chemical processes to geomaterials, this work mainly captures two of the most important phenomena of practical importance in geotechnical engineering: (1) reactive fluid transport in the pores and what happens inside of pores; and (2) solid deformation and damage response to the mechanical and chemical loads. Nowadays, especially in today's thriving development of energy geotechnical engineering, geological materials are exposed to an environment even more complex than the natural environment itself. Much research

has been carried out to analyze certain aspects of these phenomena. We have made a comprehensive review of the signs of progress, and advantages/disadvantages in Section 1.1. The present research contributes to this subdiscipline by exploring techniques for analyzing the mechanical behavior of geological materials using continuum mechanics and computational modeling methods. This dissertation provides techniques to address geotechnical engineering problems related to geomaterials exposed to mechanical and chemical erosion environments. However, it is important to note that we do not aim to provide a general solution for all numerical analysis issues, nor do we intend to replace existing numerical solutions. The following section outlines the most important technical contributions of this dissertation. We briefly introduce each contribution and refer to the corresponding sections in the dissertation for more detailed explanations.

Develop local chemical equilibrium equations based on thermodynamic principles for the pore geochemistry of reactive multi-component systems to explicitly capture mineral dissolution and precipitation processes in saturated porous media

The key feature of this contribution is that an explicit local chemical equilibrium model with consideration of key (carbon) atom conservation is developed. Via this model, a complete chemistry system of  $H_2O-CO_2-CaCO_3$  is considered, including intra-aqueous chemical reactions and kinetic rate-limiting chemical reactions. We have introduced the important progress of geochemistry into geotechnical engineering and the importance of pore geochemistry in analyzing the coupled effects on the mechanical behaviors in solid mechanics in Section 1.1. This contribution selects the key features of pore geochemistry and solid mechanics (poromechanics) to combine an explicit way to capture both updates for hydraulic conductivity properties and chemical reaction details for multi-component systems. This contribution also includes the verification and validation of the pore geochemistry performance on different initial reaction systems. Different benchmarks have been performed to confirm the model is capable of recognizing the mineral dissolution/precipitation processes occurring under different chemical conditions. Section 2.2 presents the details of derivations and formulations of this contribution.

Develop a coupled algorithm that can be incorporated into existing finite element frameworks for hydro-mechanical processes of porous media

The key feature of this contribution is that a combined monolithic-sequential solution strategy is developed. The poroelasticity theory provides a basic framework to consider the
pore pressure and displacement variations in porous media. Our in-house computational mechanics code GEOCENTRIC is capable of dealing with pore pressure and displacement coupling with a monolithic solving algorithm under saturated conditions. One of the works in our research is to introduce the local chemical equilibrium we proposed into a fluid transport equation to form a new reactive transport equation. This new reactive transport equations. The coupled strategy and solving orders are introduced in Section 2.4. The discretization for governing equations is developed for the finite element method. Details of the space and time discretization can be found in Section 2.3. Finally, simulations are carried out to verify the performance of the proposed computational framework. Section 2.4 lists all of the verification and validation results and the comparison between numerical simulations and laboratory experimental results also can be found here.

Establish crack evolution in a poroelasticity problem using the phasefield framework, enabling the integration of fracture mechanics with fluid flow and mechanical deformation

The phenomenon of crack propagation is a behavior observed in geomaterials at the macroscale, commonly applied in hydraulic engineering; however, it originates from energy release at the microscale. There are plenty of significant advancements across various methodologies and applications to simulate the crack evolution, which has been reviewed in Section 1.1. This dissertation employs the basic theory related to the phase field method but extends the classical crack evolution in the phase field method from inherently well-suited for brittle fracture to poroelasticity hydraulic fracture. The concept model and the corresponding assumptions and formulations can be found in Section 3.2. The key contribution of this part is the establishment of the connection of poroelasticity to the classical phase field method. This work follows the classical approach of a spectral decomposition of the tension-compression formulation and adds the damage parameter into the tension component. However, the evolution of the damage parameter is derived based on the poroelasticity theory. As for the reactive fluid transport in the cracking porous media, this work follows the subdomain concept and introduces the phase field damage parameter to separate the flow pressure system, treating the fluid in the reservoir and the fracture as distinct entities. The corresponding uniform mass continuity equations are given and indicators into these equations to get a compact formula. This contribution can be also found in Section 3.3.

# Extension of the local chemical equilibrium to the multi-mineral dissolution/precipitation represented by sandstone

The contribution of explicit local chemical equilibrium equations provides an approach to consider pore geochemistry, such as dissolution/precipitation of calcite, which can be extended to a more complex reaction system. The key feature of this contribution is the extension of the previous single mineral to a multi-mineral system to allow us to consider more realistic rock/soil mineral systems, such as sandstone. The intra-aqueous reactions for different mineral categories are reorganized and put into the balance of mineral mass and chemical species to form a new series of reactive transport equations. To match the different types of fluid transport due to the pressure difference in pore and fracture, the damage phase field parameter is introduced into the balance equations. This contribution can be found in Section 3.3.

#### Establish a total potential energy system considering the work done by both the fluid and the solid to capture the crack nucleation, propagation, and merging in the porous media

After establishing the crack evolution in poroelasticity and extending the acid fluid-calcite reaction model to acid fluid-multi-mineral systems, we need to bridge the constitutive response between the multi-mineral reaction system and crack evolution. The key feature of this contribution is the establishment of a total potential energy system that contains all of the workings of the fluid and solid. The potential energy comprises several components, including the dissipation of energy due to cracking, the elasticity potential energy in the bulk of the solid, the energy stored in the fracture fluid, the energy stored in the porous fluid, and the external energy source. Details of each component and the corresponding formulas can be found in Section 3.4. The constitutive response includes mass exchanges and chemical responses. The reactive fluid transport can alter the concentration distribution of chemical species and can provide feedback to the intra-aqueous system, which reflects on the source/sink terms of transport equations. The mass exchanges between fluid and solid then are directly computed by the mass fraction equations, which are further used to characterize the changes in porosity and permeability. The hydromechanical response at this stage is represented by the alterations of the elastic modulus by connecting with porosity changes. In addition, the combined chemical-mechanical damage parameter is defined as being obtained from pure mechanical damage, which is linked with the porosity changes. These contributions

are presented in Section 3.4. Finally, the implementation of the coupling scheme and numerical simulations for different verifications are provided in Section 3.5. We note that the coupling scheme in this work still follows previous contributions with the combined implicit monolithic and staggered algorithms.

#### Examination of the chemical kinetics of the dissolution mechanism in granular geomaterials under stress and geochemical reactions

Another contribution of this dissertation is related to the change in the mechanical properties. Although the constitutive response of solid minerals has been discussed, the underlying mechanisms by which chemo-mechanical interactions influence the material's mechanical properties remain unclear in the constitutive model. The key feature of this contribution is the examination of the chemical kinetics dissolution mechanism of granular geomaterials under stress and geochemical reactions from chemical potential energy aspects. Besides the local chemical equilibrium for geochemistry that we obtained previously, we introduce the chemical potential difference induced by the stress difference between rock and the surrounding fluid, which is another driving force of rock dissolution. The new complete chemical kinetics dissolution mechanism characterizes the solid mineral dissolution-transport processes and can be introduced into a material degradation function. The relevant detailed definitions and assumptions are illustrated in Section 4.

# Thermodynamic-based cross-scale model for the granular geomaterials with emphasis on stiffness degradation and bonding/debonding effects

Finally, we provide a cross-scale model to capture the evolution of material stiffness degradation and bonding/debonding effects. The key feature of this contribution is the connection between grain size and bond size evolution and the chemical kinetics dissolution mechanism. This relationship is established based on thermodynamics, considering the effects of chemical reaction rates influenced by chemical ions in the pore and the contact forces between grains and bonds. The measurement of mineral mass dissolution can then be integrated with the chemical kinetic dissolution rate and the probability density function related to grain particle sizes. The softening of the geomaterial is reflected by the mass dissolution from the chemical process and is further characterized by stiffness and debonding degradation parameters. The degradation function is introduced into a Cam-Clay-type model to derive the evolution of hyperelasticity and internal variables. This work also emphasizes methods to approximate the contact forces between grains and bonds. For a well-distributed soil specimen, the data collected to analyze the

relationship between particle size and its contribution to average effective stress presents a clear linear relationship. This linear relationship is then used to revise the impact of pressure dissolution on mineral mass dissolution. To better integrate the finite element method with the material's constitutive properties, this work also provides the algorithmic tangent operator, which can be called in each iteration at Gauss points during numerical calculations. The corresponding validations and verifications are provided in Section 4.

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## Chapter 2

# A computational framework based on explicit local chemical equilibrium for coupled chemo-hydro-mechanical effects on fluid-infiltrating porous media

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## A computational framework based on explicit local chemical equilibrium for coupled chemo-hydro-mechanical effects on fluid-infiltrating porous media

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#### Abstract

Conventionally, a finite element framework for coupled hydro-mechanical-chemical processes in porous media adopts simplified chemical reactions that consider only the superficial chemical effects of complex multiphysics mechanisms. This paper presents a novel computational framework for the geochemistry of reactive multi-component systems to explicitly capture the mineral dissolution/precipitation in saturated porous media. The results of this framework can be applied in oil recovery engineering and used to simulate production scenarios. The model is also fundamental for studying creep behavior from the perspective of the coupling effects between hydrogeochemistry. In particular, a complete chemical system of  $H_2O-CO_2-CaCO_3$  is considered, including intra-aqueous chemical reactions and kinetic rate-limiting chemical reactions. Additionally, an algorithm is proposed such that the complete chemistry system is scalable for various chemical reactions and is easily incorporated into existing finite element frameworks for hydromechanical processes of porous media. This complete chemical system is implemented to establish local chemical equilibrium. The geochemical reactive transport equations are then sequentially coupled with the balance laws, allowing the simulation of coupling among fluid advection-diffusion, solid deformation, chemical concentration advectiondiffusion, intra-aqueous chemical reaction, and kinetic rate-limiting chemical reactions. Phenomenological relations for porosity and permeability changes with mineral saturation in solutions are employed. We first verify the proposed framework's capability to capture the advection-diffusion of different chemical species under steady-state and transient conditions. Then, a consolidation problem subject to chemical reactions is presented to further demonstrate the capabilities of the proposed computational framework.

**Keywords:** Finite Element Method, Geochemistry, Chemo-hydro-mechanical coupling, Poroelasticity, Reactive flow.

#### 2.1 Introduction

Subsurface chemo-mechanical alterations in porous media have a significant impact on various issues including groundwater contamination, underground energy recovery, and long-term infrastructure stability (Akono et al., 2019). This can be seen in applications like carbon dioxide capture and storage (CCS) (Davidson and Metz, 2005) and the oil and gas industry. For instance, the dissolution of  $CO_2$  into the resident brine can accelerate rock-brine- $CO_2$  interactions, leading to mineral dissolution/precipitation and clay fabric alteration (Liu et al., 2020; Tang et al., 2021; Xu et al., 2020). Therefore, a profound understanding of such alterations in petrophysical and geochemical properties associated with  $CO_2$ -related reactions is critical for accurately investigating the coupled hydro-mechanical-chemical processes in porous media.

Many researchers have leveraged laboratory tests to explore the chemical impacts on the mechanical responses of geomaterials. Zinsmeister et al. (2013) and Bemer and Lombard (2010) conducted experiments with limestone to observe the mechanical weakening phenomenon due to acid-rock or  $CO_2$ -rock interactions. These static experiments revealed that changes in porosity, micro-cracking, and decrements in drained elastic moduli and shear strength may have caused the weakening problem. However, different phenomena were observed by Rimmelé et al. (2010), who found no clear change in mechanical properties when Lavoux limestone was exposed to  $CO_2$  (scCO<sub>2</sub>). It was suggested that  $CO_2$ -induced mechanical weakening should be observed over long time scales, which is different from acid-induced alteration. Further experimental studies revealed the importance of pore fluid geochemistry. Rathnaweera et al. (2015) concluded that fluid chemistry was critical to the mechanical responses of porous media through experiments on quartz-rich sandstone saturated with brine containing varying compositions of  $CO_2$  to

induce geochemical reactions. Hu et al. (2017) further confirmed the strong influence of pore fluid chemistry on sandstone, emphasizing the importance of lithology, morphology, and reservoir conditions in understanding the  $\rm CO_2$ -induced geomechanical alterations of heterogeneous porous media.

Although laboratory tests provide a direct way to investigate subsurface mechanical responses due to chemo-mechanical coupling effects, some micro-phenomena, such as pore fluid chemistry and kinetics, are difficult to capture. Additionally, most experiments for geochemical reactions in porous media usually take a long time, which is a critical limitation. An alternative approach is theoretical modeling of coupled chemo-hydromechanics. Based on the inter-granular pressure solution (IPS) mechanism, some constitutive models have been developed for granular porous media to capture chemical degradation (Nova et al., 2003; Pietruszczak et al., 2006; Navarro et al., 2010; PINYOL et al., 2011; Ciantia, 2018). The introduction of micro-mechanisms allowed the models to capture phenomena that were difficult to observe in experiments. However, the reason for stiffness weakness was still not fully investigated. Recently, a coupled damage-plasticity model was developed to describe the macroscopic mechanical response of porous media, capturing brittle, brittle-ductile transition, and ductile responses (Mir et al., 2018). However, a limitation of that model is the underestimation of the micro-mechanisms in deformation and energy dissipation, where chemical degradation is not directly introduced in the formulation.

Compared with laboratory tests and theoretical approaches, computational models can accommodate multiphysics to capture chemical effects from a broader perspective. There exist various mature numerical simulators used in geofluid and geomechanics, such as the TOUGH series, ECLIPSE, and FYNAFLOW for reservoir flow simulation, and FLAC3D, STARS for geomechanical simulation (Akono et al., 2019). However, this mature software lacks detailed consideration of interactions between the fluid and reservoir rock, especially regarding coupled chemo-mechanical alteration effects.

To date, several studies have made contributions to simple and complex coupling between chemical reaction flow and geomechanics (Kadeethum et al., 2021; Choo and Sun, 2018; Chaudhuri et al., 2013; Schuler et al., 2020). For example, Fernandez-Merodo et al. (2007) proposed a solution strategy to couple dilute solute transport and porous material, studying the evolution of material degradation and the mechanical response of the solid. They simplified the transport equations by neglecting the diffusive term and treated chemical reactions as first-order global reactions without intra-aqueous reactions. Roshan and Rahman (2011) developed a fully-coupled, chemo-poroelastic model that integrated chemo-hydro-mechanical processes. It revealed the relationships between solute transfer and chemical equilibrium. However, the model did not include refined approaches to capture chemical reactions, particularly regarding intra-aqueous and kinetic reactions. Amir and Kern (2017) developed an efficient global approach for coupling transport and chemistry based on the Newton-Krylov method. The model effectively solved the intra-aqueous chemical equilibrium and fluid transport. Additionally, block preconditioners for the linear systems were used to accelerate the convergence of the Krylov method and reduce CPU time. However, the proposed framework could not handle multidimensional conditions and kinetic reactions. In summary, most existing frameworks for coupled hydro-mechanical-chemical processes in porous media adopt simplified reactive flow and transport or reduced chemical systems based on empirical relationships.

The main objectives of this study are (1) to establish both intra-aqueous and kinetic geochemistry theory to describe a complete chemical reaction system and (2) to develop a finite element framework that can easily incorporate more comprehensive interactions between displacement, pressure, and transport variables. As such, the coupling mechanism among fluid intra-aqueous reactions, fluid-solid kinetics, fluid advection-diffusion, and solid mechanics is captured. In particular, we introduce a geochemistry sub-framework that distinctively captures the chemistry of the  $H_2O-CO_2-CaCO_3$  system. By considering the rate law for mineral dissolution and precipitation reactions, and combining component equilibrium chemistry with fluid transport inside the porous media, we track changes in porosity and permeability over time, which is vital to the mechanical responses.

Specifically, calcite is selected as a representative mineral in the  $H_2O-CO_2-CaCO_3$ system because of its active preference for geofluids. The complete ternary system is established by preserving the local equilibrium of chemical species, including Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>, and H<sup>+</sup>, to account for the dissolution/precipitation of calcite. Based on the local chemical concentration equilibrium, the reactive transport systems for each species and the liquid phase of carbon dioxide (CO<sub>2</sub><sup>o</sup>) are established. The geochemical reactive transport equations are then sequentially coupled with the balance laws, allowing for the simulation of fluid advection-diffusion, solid deformation, chemical concentration advection-diffusion, intra-aqueous chemical reactions, and kinetic rate-limiting chemical reactions. This approach enables us to capture the composition of pore chemistry as fluid infiltration and solid mineral dissolution/precipitation progress, and further capture the mechanical behavior with composition changes. The resulting framework has several potential engineering applications. The proposed model's capability to capture CO<sub>2</sub> reactions with pore fluid and mineral composition can evaluate changes in the mechanical properties of the injection and caprock layers, which is important for the long-term injection of  $CO_2$  in mature oilfield recovery applications (Zhao and Jha, 2019; Zheng et al., 2021). The synthetic technical indexes obtained from the model, such as effective stress, pore-scale deformation, and reservoir pore pressure, are important for estimating alternating injection and production scenarios (Tran and Jha, 2021). Furthermore, the model is fundamental for studying the creep behavior of reservoirs exposed to  $CO_2$ -acidified brine. This is attributed to the comprehensive understanding of the influence of fluid-rock chemo-mechanical interactions on the long-term and time-dependent mechanical properties provided by our model (Akono et al., 2020).

We further note that the proposed geochemistry sub-framework is scalable to accommodate different chemical systems and can be easily coupled with existing frameworks for saturated porous media without significant computational cost. The resulting framework may provide a clearer picture when analyzing fluid pressure and solid displacement due to the dissolution/precipitation of calcite. The verification examples confirm that fluid advection-diffusion results are consistent between analytical and numerical solutions. A chemical benchmark problem is designed to calibrate the accuracy of the geochemistry solver. Finally, Terzaghi's two-dimensional consolidation is revisited to showcase the capability of the proposed computational framework. In this paper, we focus on alterations of hydraulic properties related to geochemistry. Thermal effects on poromechanics and fluid properties are beyond the scope of this research. Future work will consider this aspect.

This paper is organized as follows. Section 2.2 summarizes geochemistry models used to capture the reactive multi-component systems for dissolution/precipitation. In Section 2.3, we present the finite element implementation of the hydro-chemo-mechanical model that simulates the coupled behavior of a reactive-flow saturated porous media. The coupling scheme of geochemistry and mechanics is given in Section 2.4, while numerical examples are presented in Section 2.5 to validate and showcase the performance of our model. Finally, the conclusion of this study is presented in Section 2.6. As for notations and symbols, bold-faced letters express tensor (including vectors that are one-dimensional tensors); the symbol '.' denotes a single contraction of adjacent indices of two tensors (e.g.,  $\mathbf{a} \cdot \mathbf{b} = a_i b_i$  or  $\mathbf{c} \cdot \mathbf{d} = c_{ij} d_{jk}$ ), while the symbol ':' denotes a double contraction of adjacent indices of tensors (e.g.  $\mathbb{C} : \boldsymbol{\epsilon} = C_{ijkl} \epsilon_{kl}$ ). As for sign conventions, unless specified otherwise, we consider the direction of the tensile stress and dilative pressure as positive.

### 2.2 Geochemistry of reactive multi-component systems for dissolution/precipitation porous media

This section presents the geochemistry theory that captures gas-liquid, intra-liquid, and liquid-solid chemical dissolution/precipitation in saturated porous media. First, background information is introduced to address the practical engineering aspects of the representative system and chemical reaction equations. We then present the chemical mass-action equations, followed by a detailed description of aqueous reactions equilibrium and solid rate-limiting kinetic reactions. Finally, the coupled chemo-mechanical alteration of porosity and permeability due to the dissolution/precipitation mechanism is described.

#### 2.2.1 Background

The equilibrium of aqueous systems and the kinetics between reactive chemical components and the solid matrix are important subjects in the hydrogeochemical field. Among the complex chemical reactions, the  $H_2O-CO_2-CaCO_3$  ternary system is one of the typical systems used to study the acidification of carbonate porous media. Application areas, including reservoir engineering and  $CO_2$  geological storage, focus on significant changes in macroscopic properties, such as porosity and permeability. In our study, we focus on the contributions of geochemistry to these changes under isothermal conditions. These changes may trigger potential risks to the porous media, such as a reduction in the integrity of the caprock. Therefore, accurate and efficient models to simulate the dissolution/precipitation processes in natural porous media are essential for evaluating the long-term stability and maintenance of infrastructure. The overall reaction formula of the  $H_2O-CO_2-CaCO_3$  ternary system is as follows:

$$\operatorname{CaCO}_3 + \operatorname{CO}_2 + \operatorname{H}_2 \operatorname{O} \longleftrightarrow \operatorname{Ca}^{2+} + 2\operatorname{HCO}_3^{-}.$$
 (2.1)

Interested readers are referred to Kaufmann and Dreybrodt (2007) for the establishment of this system.

The chemical reactions related to the dissolution and precipitation of calcite in an open or closed system concerning  $CO_2$  are explained below. It is worth noting that an open system means the gas phase of  $CO_2$  is continuously replenished in the system, which corresponds to a continuous  $CO_2$  injection in engineering situations. Conversely, if the gas phase of  $CO_2$  is completely dissolved into the aqueous phase, this kind of system is called a closed system. The intermediate system is between the open and closed systems.

The chemical reaction processes are mainly characterized by Eqs. (2.2) to (2.9) as follows:

$$\mathrm{H}_{2}\mathrm{O} \stackrel{K_{W}}{\longleftrightarrow} \mathrm{H}^{+} + \mathrm{OH}^{-}, \tag{2.2}$$

$$\operatorname{CO}_2 \xleftarrow{K_H} \operatorname{CO}_2^0,$$
 (2.3)

$$\operatorname{CO}_2^0 + \operatorname{H}_2 O \stackrel{k_1}{\longleftrightarrow} \operatorname{H}_2 \operatorname{CO}_3^0 \stackrel{K_5}{\longleftrightarrow} \operatorname{H}^+ + \operatorname{HCO}_3^-,$$
 (2.4)

$$\operatorname{CO}_2^0 + \operatorname{OH}^- \xleftarrow{k_2} \operatorname{HCO}_3^-,$$
 (2.5)

$$\mathrm{HCO}_{3}^{-} \stackrel{K_{2}}{\longleftrightarrow} \mathrm{H}^{+} + \mathrm{CO}_{3}^{2-}, \qquad (2.6)$$

$$\operatorname{CaCO}_{3}^{0} + \operatorname{H}^{+} \underset{\kappa_{4'}}{\overset{\kappa_{1}}{\longleftrightarrow}} \operatorname{Ca}^{2+} + \operatorname{HCO}_{3}^{-}, \qquad (2.7)$$

$$CaCO_3^0 + H_2CO_3^0 \xleftarrow{\kappa_2}_{\kappa_4 \prime \prime} Ca^{2+} + 2HCO_3^{-}, \qquad (2.8)$$

$$\operatorname{CaCO}_{3}^{0} + \operatorname{H}_{2}O \xleftarrow{\kappa_{3}}{} \operatorname{Ca}^{2+} + \operatorname{CO}_{3}^{2-} + \operatorname{H}_{2}O.$$

$$(2.9)$$

The first reaction describes the dissolution of water into hydrogen and hydroxide ions; the second reaction is the physical dissolution of carbon dioxide in water; the third and fourth reactions are the conversion of carbon dioxide into hydrogen and bicarbonate, depending on the pH value of the solution. Sometimes,  $H_2CO_3^0$  can be written as the total amount of  $CO_2^0$  available ( $H_2CO_3^* = CO_2^0 + H_2CO_3^0$ ). The fifth reaction is the dissociation of bicarbonate into hydrogen and carbonate ions, and the sixth to eighth reactions are all related to the dissolution of carbonate, which also depends on the pH value. Note that the equilibrium constants are denoted in the above equations. Capital letters are used to indicate fast intra-aqueous reactions and lowercase letters denote reaction-rate constants for slow kinetic reactions.

#### 2.2.2 Chemical mass-action equations

The transformation of substances in chemical reactions is governed and conserved by chemical mass-action equations. We note that for the ternary system H<sub>2</sub>O-CO<sub>2</sub>-CaCO<sub>3</sub>, all chemistry calculations neglect ion pairing impacts.  $[X_i] (mol/m^3)$  denotes the concentration of species  $X_i$ , and  $(X_i)$  denotes its activity, while  $\gamma_i$  represents the activity coefficient. Activities and concentrations are related to each other (Garrels, 1965),

$$(X_i) = \gamma_i [X_i]. \tag{2.10}$$

Firstly, the dissolution of  $CO_2$  into a solution can be described as the equilibrium between gas phase  $CO_2$  and liquid phase  $CO_2^{0}$ ,

$$(CO_2^{\ 0}) = K_{\rm H} p_{\rm CO_2},$$
 (2.11)

where  $K_H$  is Henry's constant.  $p_{\text{CO}_2}$  is the partial pressure of  $\text{CO}_2$ , which reacts to form cabonic acid. Note again that  $\text{CO}_2^{\ 0}$  denotes the aqueous phase of  $\text{CO}_2$  dissolved in water, and the mass-action equation is:

$$(\mathrm{CO}_2^{\ 0}) = K_0(\mathrm{H}_2\mathrm{CO}_3^{\ 0}).$$
 (2.12)

If we consider carbonate acid rewritten as  $CO_2^{0}$ , then

$$(\mathrm{CO}_2^{\ 0}) = \left(1 + \frac{1}{K_0}\right)^{-1} (\mathrm{H}_2 \mathrm{CO}_3^*),$$
 (2.13)

and the carbonate acid dissociates into  $\mathrm{H}^+$  and  $\mathrm{HCO}_3^-,$  then

$$\frac{(\mathrm{H}^+)(\mathrm{HCO}_3^-)}{\mathrm{H}_2\mathrm{CO}_3^*} = K_1.$$
(2.14)

In addition,  $\mathrm{HCO}_3^{\,-}$  also dissociates into  $\mathrm{H}^+$  and  $\mathrm{CO}_3^{\,2-}$  as follows,

$$\frac{(\mathrm{H}^+)(\mathrm{CO}_3^{\ 2^-})}{(\mathrm{HCO}_3^{\ -})} = K_2.$$
(2.15)

Finally, we also consider the dissociation of water as,

$$(\mathrm{H}^+)(\mathrm{OH}^-) = K_W.$$
 (2.16)

The aforementioned mass-action equilibrium constants are all derived from laboratory experimental results. In this study, the parameters used to calculate mass actions for the numerical experiments are listed in Table 2.1.

Parameter $\log K_H$ $[mo$ $\log K_W$ $[\gamma$ $\log K_S$ $[\gamma$ $K_0$ $K_1$ $K_1$ $\log K_2$ $\log K_5$ $\log K_6$			
$\log K_H$ [mo $\log K_W$ [ $_1$ $\log K_S$ [ $_1$ $K_0$ $K_1$ $\log K_5$ $\log K_6$	Unit	${f Relationships}$	References
$\log K_W$ [ $j$ $\log K_S$ [ $j$ $K_0$ $K_1$ $\log K_2$ $\log K_5$ $\log K_6$	$l^{-1}atm^{-1}$	$108.3865 + 0.01985076T - 6919.53T^{-1} - 40.45154\log(T) + 669365T^{-2}$	Plummer and Busenberg (1982)
$\log K_S$ [ $\eta$ $K_0$ $K_1$ $\log K_2$ $\log K_5$ $\log K_6$	$nol^{2}l^{-2}$ ]	$22.801 - 0.010365T - 4787.3T^{-1} - 7.1321 \log(T)$	Wagner and Kretzschmar (2008)
$egin{array}{c} K_0 & K_1 & \ \log K_2 & \ \log K_5 & \ \log K_6 & \ \end{array}$	$nol^{2}l^{-2}$ ]	$8.15087602 + 0.0136633623T_C - 3.5812701E^{-5}T_C^2$	This study
$egin{array}{c} K_1 \ \log K_2 \ \log K_5 \ \log K_6 \end{array}$	-	$K_5/K_6$	Plummer and Busenberg (1982)
$\log K_2$ $\log K_5$ $\log K_6$	$noll^{-1}$	$K_5 K_6/(K_5+K_6)$	Plummer and Busenberg (1982)
$\log K_5$ $\log K_6$	$noll^{-1}$	$-107.8871 - 0.03252849T + 5151.79T^{-1} + 38.92561\log(T) - 563713.9T^{-2}$	Plummer and Busenberg (1982)
$\log K_6$	$noll^{-1}$	$1.707E^{-4}$	Plummer and Busenberg (1982)
,	$noll^{-1}$	$-356.3094 - 0.06091964T + 21834.37T^{-1} + 126.8339\log(T) - 1684915T^{-2}$	Plummer and Busenberg (1982)
$\log \kappa_1$	$cms^{-1}]$	$0.198 - 444.0T^{-1}$	Plummer et al. (1978)
$\log \kappa_2$	$cms^{-1}]$	$2.84 - 2177.0T^{-1}$	Plummer et al. (1978)
$\log \kappa_3 \qquad [mm]$	$plcm^{-2}s^{-1}]$	$-5.86 - 317.0T^{-1}(T_C < 25), -1.10 - 1737.0T^{-1}(25 < T_C < 48)$	Plummer et al. (1978)
$\log \kappa_{4s}$ $[cm^4]$	$nmol^{-1}s^{-1}]$	$\begin{array}{l} -2.375 + 0.0252 T_{C} + 0.56 (-\log(p_{\mathrm{CO_2}}) - 1.3)) (p_{\mathrm{CO_2}} < 0.05 a t m), \\ -2.375 + 0.0252 T_{C} (p_{\mathrm{CO_2}} > 0.05 a t m) \end{array}$	Kaufmann and Dreybrodt (2007)
$\kappa_a$ [ $l($	$mols)^{-1}]$	$\kappa_1^-(\gamma_{\rm H}^+\gamma_{\rm HCO_3^-})/K_5$	

\*  $T_C$  is temperature using Celsius while T is temperature using Kelvin. The Unit of p is atm.

TABLE 2.1: Equilibrium parameters used in this numerical study

#### 2.2.3 Aqueous reactions equilibrium

To establish aqueous reaction equilibrium using chemical mass-action equations, ionic strength, and ion activity must be determined first. Then, the chemical equilibrium can be established, followed by the carbon atom conservation law.

#### 2.2.3.1 Ionic strength and ion activity

Before solving for ionic activity, it is essential to determine the ionic strength of a solution. According to the definition of ionic strength (Sastre de Vicente, 2004), it is given by:

$$I = \frac{1}{2} \sum_{i} z_i^2 [X_i], \qquad (2.17)$$

where I is ionic strength  $(molm^{-3})$ , and  $z_i$  is the ionic charge. If this formula is applied to the system of this study, then:

$$I = \frac{1}{2} \left( 4 [\text{Ca}^{2+}] + [\text{H}^+] + [\text{OH}^-] + 4 [\text{CO}_3^{2-}] + [\text{HCO}_3^{--}] \right).$$
(2.18)

The ion activity coefficients are described by Debye–Hückel theory, which is sufficiently precise for very dilute solutions. Following the work of Huebner (1970), the ion activity coefficients are given by the WATEQ Debye-H"uckel equation (B dot activity model):

$$\log(\gamma_i) = -\frac{Az_i^2\sqrt{I}}{1+Ba_i\sqrt{I}} + b_iI,$$
(2.19)

where  $a_i(m)$  and  $b_i(m^3mol^{-1})$  are ion-specific parameters, and  $A(\sqrt{(m^3mol^{-1})})$  and  $B(\sqrt{m^3mol^{-1}m^{-1}})$  are temperature-dependent coefficients. The specific values are listed in Table 2.2.

TABLE 2.2: Coefficients for the extended Debye-Hückel equation

Ions	$a_i(10^{-10}m)$	$b_i(lmol^{-1})$	$z_i$
$\mathrm{Ca}^{2+}$	5.0	0.165	+2
$\mathrm{HCO}_3^-$	9.0	-	-1
$\mathrm{CO}_3^{\ 2-}$	5.4	-	-2
$OH^-$	5.4	-	-1

Ions	$a_i(10^{-10}m)$	$b_i(lmol^{-1})$	$z_i$
H <sup>+</sup>	3.5	-	+1
A	$0.4883 + 8.074E^{-4}T_C$		
В	$0.3241 + 1.6E^{-4}T_C$		
$\overline{\mathrm{CO}_2^0}$	$10^{0.1I}$		
$H_2CO_3^*$	$10^{0.1I}$		

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TABLE 2.2: Coefficients for the extended Debye-Hückel equation

 $T_C$  is temperature in Celsius.

(continued)

Neutral species  $\text{CO}_2^0$  and  $\text{H}_2\text{CO}_3^*$  are directly calculated by the equation in this table.

#### 2.2.3.2 Equilibrium chemistry

This section provides formulas to determine the chemical composition of the  $CO_2$ ,  $H_2O$ , and  $CaCO_3$  system during the dissolution of calcite under general conditions. The conservation of carbonate species is considered first. The total amount of carbon in the system is calculated based on the concentrations of all carbon-containing species in the liquid and gas phases. Initially, we consider the amount of carbon atoms in the pure  $H_2O-CO_2$  system, before the dissolution of calcite. After dissolving calcite, the initial system gains an additional carbon atom from the release of CaCO<sub>3</sub>. Once the initial partial  $CO_2$  pressure and the Ca<sup>2+</sup> concentration of the solution are known, the chemical composition of the solution can be determined. In this case, the carbon atom conservation equation is:

$$M_T = ([\mathrm{Ca}^{2+}] + [\mathrm{HCO}_3^{-}]_i + [\mathrm{H}_2\mathrm{CO}_3^{*}]_i + [\mathrm{CO}_3^{2-}]_i)V_l + [\mathrm{CO}_2]_iV_g$$
(2.20)

$$= ([\text{HCO}_{3}^{-}] + [\text{H}_{2}\text{CO}_{3}^{*}] + [\text{CO}_{3}^{2-}])V_{l} + [\text{CO}_{2}]V_{g}, \qquad (2.21)$$

where  $V_l$  and  $V_g$  are the volume of liquid solution and gas, respectively. The blank bracket []<sub>i</sub> denotes the initial H<sub>2</sub>O-CO<sub>2</sub> system prior to dissolution.

The next equation is for electroneutrality, which reads:

$$2[Ca2+] + [H+] = [HCO3-] + 2[CO32-] + [OH-].$$
(2.22)

Based on the relationships in Eqs. (2.14) and (2.15), subtracting Eq. (2.21) from Eq. (2.20) yields:

$$[\operatorname{Ca}^{2+}] + [\operatorname{H}^+] - v - \frac{K'_W}{[\operatorname{H}^+]} + \left(w[\operatorname{H}^+] - \frac{K'_2}{[\operatorname{H}^+]}\right)[\operatorname{HCO}_3^-] = 0.$$
(2.23)

Furthermore, multiplying Eq. (2.20) by 2 and subtracting Eq. (2.23) gives:

$$2v - [\mathrm{H}^+] + \frac{K'_W}{[\mathrm{H}^+]} = [\mathrm{HCO}_3^-](1 + 2w[\mathrm{H}^+]), \qquad (2.24)$$

where the following definitions hold:  $v = f[H_2 CO_3^*]_i + [HCO_3^-]_i; K'_W = \frac{K_W}{\gamma_H \gamma_{OH}};$  $f = 1 + \frac{(1+1/K_0)^{-1}}{K_H RT}x; x = \frac{V_g}{V_l}; K'_2 = \frac{K_2 \gamma_{HCO_3}}{\gamma_H \gamma_{CO_3}}; w = f \frac{\gamma_H \gamma_{HCO_3}}{K_1}.$ 

After combining Eqs. (2.23) and (2.24), we obtain a fourth-order polynomial in hydrogen ion concentration that can be solved numerically.

$$\left[\operatorname{Ca}^{2+}\right] + \left[\operatorname{H}^{+}\right] - v - \frac{K'_{W}}{\left[\operatorname{H}^{+}\right]} + \left(w[\operatorname{H}^{+}] - \frac{K'_{2}}{\left[\operatorname{H}^{+}\right]}\right) \left(2v - \left[\operatorname{H}^{+}\right] + \frac{K'_{W}}{\left[\operatorname{H}^{+}\right]}\right) \left(1 + 2w[\operatorname{H}^{+}]\right)^{-1} = 0.$$
(2.25)

Note that  $x = V_g/V_l$  controls the conditions of the system, where the x value affects on f. Therefore, if f = 0, the system is a closed system, and all of the CO<sub>2</sub> gas dissolves into the liquid solution. Otherwise, if  $f = \infty$  (typically set as 10<sup>5</sup>), the system is considered an open system, where CO<sub>2</sub> continuously dissolves into the liquid solution. Note that Eq. (2.24) can be solved using the bisection method. In other words, once [H<sup>+</sup>] is known, [HCO<sub>3</sub><sup>-</sup>] can be solved by Eq. (2.23). Then [OH<sup>-</sup>], [CO<sub>3</sub><sup>2-</sup>], and [H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>] can be solved by mass action using Eqs. (2.11)~(2.16). Once the chemical concentrations are updated, the kinetic transformations described by Eqs. (2.2) to (2.9) can be determined. The chemical reaction rate  $S_R$  can be defined to capture the creation or destruction rate of corresponding chemical species. This kinetic reaction rate acts as a specific source or sink term in the transport Eq. (2.33).

#### 2.2.4 Solid rate-limiting kinetic reactions

The reaction of minerals is relatively slow compared to intra-aqueous reactions. In this study, we assume that mineral reactions do not reach equilibrium instantaneously, as the evolution of calcite is a process occurring over both space and time. According to the transition state theory, elemental chemical reactions can be quantitatively described, and

TABLE 2.3: Kinetic reaction rate  $S_R$  for advection-diffusion-reaction equation

Species	$S_R$
$\overline{\mathrm{CO}_2}$	$\kappa_1^+[\mathrm{CO}_2^0] - \kappa_a[\mathrm{H}^+][\mathrm{HCO}_3^-] + \kappa_2^+[\mathrm{CO}_2^0][\mathrm{OH}^-] - \kappa_2^-[\mathrm{HCO}_3^-]$
$\mathrm{Ca}^{2+}$	$\kappa_{1}[\mathrm{H}^{+}][\mathrm{CaCO}_{3}^{0}] + \kappa_{2}[\mathrm{H}_{2}\mathrm{CO}_{3}^{*}][\mathrm{CaCO}_{3}^{0}] + \kappa_{3}[\mathrm{CaCO}_{3}^{0}] - \kappa_{4}[\mathrm{Ca}^{2+}][\mathrm{HCO}_{3}^{-}]$
$\mathrm{HCO}_3^{-}$	$-\kappa_1^+[\text{CO}_2^0] + \kappa_a[\text{H}^+][\text{HCO}_3^-] - \kappa_2^+[\text{CO}_2^0][\text{OH}^-] + \kappa_2^-[\text{HCO}_3^-]$
$\mathrm{CO}_3^{\ 2-}$	$\kappa_3 [{ m CaCO}_3^{\ 0}] - \kappa_4^{\prime\prime\prime} [{ m Ca}^{2+}] [{ m CO}_3^{\ 2-}]$
$\mathrm{OH}^-$	$-k^{2+}[\mathrm{CO}_{2}^{\ 0}][\mathrm{OH}^{-}] + k^{2-}[\mathrm{HCO}_{3}^{-}]$
$\mathbf{H}^+$	$-\kappa_1 [CaCO_3^{\ 0}][H^+] + \kappa'_4 [Ca^{2+}][HCO_3^{-}]$

\* Here  $\kappa_4 = \kappa'_4 + \kappa''_4[\text{HCO}_3^-] + \kappa'''_4[\text{OH}^-].$ 

the reaction rates can be expressed as follows (Kestin et al., 1981):

$$\gamma_{\beta} = \kappa_{\beta} \dot{A}_{\beta} \left( 1 - \frac{Q_{\beta}}{K_{eq_{\beta}}} \right), \qquad (2.26)$$

where  $\gamma_{\beta}$  is the rate of reaction  $(mol \cdot m^{-3} \cdot s^{-1})$ ,  $\kappa_{\beta}$  is the rate constant  $(mol \cdot m^{-2} \cdot s^{-1})$ ,  $\dot{A}_{\beta}$  is the reactive surface area  $(m^2/m^3)$ ,  $Q_{\beta}$  is the activity product, and  $K_{eq_{\beta}}$  is the equilibrium constant.

The activity product is always expressed as  $Q_{\beta} = \prod_{i=1}^{n_{aq}} (X_i)^{v_{i\beta}}$ , where  $(X_i)$  is the activity of one product and  $v_{i\beta}$  is the corresponding stoichiometry of the product. The product does not involve the activities of minerals, as they are equal to unity. The chemical equilibrium constant  $K_{eq_{\beta}}$  for calcite is listed as  $\log K_S$  in Table 2.1. The ratio  $(Q_{\beta}/K_{eq_{\beta}})$  is known as the saturation index of the mineral reaction. If  $Q_{\beta}/K_{eq_{\beta}} > 1$ , the aqueous solution is the supersaturated solution, leading to the precipitation of the mineral, characterized by a positive reaction rate in this study. For  $Q_{\beta}/K_{eq_{\beta}} < 1$ , the aqueous solution is the unsaturated solution, leading to the dissolution of the mineral, characterized by a negative reaction rate in this study. Generally, the rate constants in Eq. (2.25) are reported as functions of temperature. Here, we employ the modified Arrhenius equation (Laidler, 1984) as follows:

$$\kappa_{\beta} = k_{\beta,0} \exp\left\{-\left[\frac{E_{a\beta}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]\right\},\tag{2.27}$$

where  $k_{\beta,0}$  is the rate constant for mineral surface reaction  $\beta$  at the reference temperature  $T_0 \ (mol/m^2s), E_{a\beta} \ (J/mol)$  is the activation energy, and R is the gas constant.

#### 2.2.5 Solid porosity-permeability changes

The dissolution and precipitation reactions of minerals affect the mechanical properties of porous media. This study mainly focuses on porosity, reaction site surface area, and intrinsic permeability of the porous media. Thus, this section briefly introduces several relationships that reflect these chemo-mechanical effects. The reactive surface area  $\hat{A}_{\beta}$  is an important parameter that reflects the reaction rate. The following equation is used to calculate the reactive surface area based on the change in the moles of minerals through dissolution or precipitation (Nghiem et al., 2004):

$$\hat{A}_{\beta} = \hat{A}^0_{\beta} \frac{N_{\beta}}{N^0_{\beta}},\tag{2.28}$$

where  $\hat{A}^0\beta$  is the reactive surface area of the mineral at the initial time,  $N\beta$  is the mole number of mineral  $\beta$  per unit grid block volume at the current time, and  $N^0_\beta$  is the mole number of mineral  $\beta$  per unit grid block volume at the initial time.

Regarding the void volume of the porous media, mineral dissolution or precipitation affects the rock porosity in (Nghiem et al., 2004) as follows:

$$\hat{\phi}^* = \phi^* - \sum_{\beta=1}^{N_m} \left\{ \frac{N_\beta}{\rho_\beta} - \frac{N_\beta^0}{\rho_\beta} \right\},$$
(2.29)

$$\phi = \hat{\phi}^* \left[ 1 + c_\phi (p - p_0) \right], \tag{2.30}$$

where  $\phi$  is the porosity,  $\phi^*$  is the reference porosity without mineral precipitation or dissolution (the initial porosity), and  $\hat{\phi}^*$  is the updated porosity.  $N_{\beta}$  is the total moles of mineral  $\beta$  per bulk volume at the current time,  $N_{\beta}^0$  is the total moles of mineral  $\beta$  per bulk volume at the initial time,  $\rho_{\beta}$  is the mineral molar density and  $c_{\phi}$  is compressibility of matrix, and  $p_0$  is the reference pressure.

This study adopts the Kozeny-Carman equation, which is widely used in models describing changes in porosity and permeability due to mineral dissolution/precipitation and biofilm accumulation (Hommel et al., 2018). Accordingly, the absolute permeability change is characterized by the Kozeny-Carman equation (Carman, 1937) as follows:

$$\frac{k}{k_0} = \left(\frac{\phi}{\phi^0}\right)^3 \left(\frac{1-\phi^0}{1-\phi}\right)^2,\tag{2.31}$$

where  $k^0$  and  $\phi^0$  are the initial absolute permeability and porosity, respectively.

#### 2.3 Finite element implementation

This section presents the implementation of the finite element method to solve the problems proposed for chemically degraded fluid-saturated geomaterials within the framework of infinitesimal strain theory. We start with the strong and weak forms of the governing equations, followed by the material models for the solid and fluid constituents. The spatial and temporal discretizations, as well as the linearization process, are also discussed. Finally, the matrix formulation of the system associated with linearization is provided.

#### 2.3.1 Governing equations

This study considers a two-phase mixture consisting of a solid matrix and a saturating fluid, both of which are assumed to be incompressible. The model focuses on mass exchange between the solid and fluid. No energy exchange the solid and the fluid is accounted. Therefore, the total system is regarded as a quasi-static isothermal system. The chemical species in this system are transported by the fluid and react with the minerals constituting the solid matrix. Both advection and diffusion effects are considered during fluid transport. The local forms of the balance of linear momentum, balance of mass, and balance of chemical species are introduced below:

$$\nabla \cdot (\boldsymbol{\sigma}' - p\boldsymbol{I}) + \rho \boldsymbol{g} = \boldsymbol{0}, \qquad (2.32)$$

$$\nabla \cdot \dot{\boldsymbol{u}} + \nabla \cdot \tilde{\boldsymbol{v}} = 0, \qquad (2.33)$$

$$\phi \dot{c}_i + \nabla \cdot (D_i \nabla c_i) + \nabla \cdot (\tilde{\boldsymbol{v}}_{c_i}) = S_{si} + S_{Ri}.$$
(2.34)

In Eq. (2.32),  $\boldsymbol{\sigma}'$  denotes the effective Cauchy stress tensor. p is the excess pore pressure.  $\boldsymbol{I}$  is the second-order unit tensor, also known as the Kronecker tensor.  $\rho$  is the buoyant density of the mixture, which includes both the solid matrix and the saturating fluid.  $\boldsymbol{g}$  is the gravity acceleration vector. In the continuity Eq. (2.33),  $\boldsymbol{u}$  is the displacement field of the solid matrix.  $\tilde{\boldsymbol{v}}$  is the seepage (Darcy) velocity, characterizing the average relative velocity of seepage per unit total area. In Eq. (2.34),  $\phi$  indicates porosity, and  $c_i$  is the chemical concentration, where the subscript *i* denotes different chemical species (including  $CO_2^{0}$ ,  $Ca^{2+}$ ,  $HCO_3^{-}$ ,  $CO_3^{2-}$ ,  $H^+$ , and  $OH^-$ ), to distinguish the transport equations of different species. The weak form and variational formulation will adhere to the subscript convention defined here.  $D_i$  is the corresponding diffusivity.  $S_{si}$  is the pure source term, which represents the creation or destruction rate of the chemical field.  $S_{Ri}$  describes the creation or destruction rate of the transported chemical species as a reaction, which is given in Table 2.3. Before solving the above equations, it is essential to incorporate the constitutive equations of the solid matrix and saturating fluid. Here, we discuss only the general form of the fluid and solid constitutive relations. Eq. (2.32) establishes the equilibrium equation in terms of the excess pressure, not the total pressure. Thus, the seepage velocity is generalized according to Darcy's law as follows:

$$\tilde{\boldsymbol{v}} = -\frac{1}{\nu}\boldsymbol{\kappa} \cdot \nabla p = -\frac{1}{\rho_f g} \boldsymbol{K} \cdot \nabla p, \qquad (2.35)$$

where  $\kappa$  is permeability tensor defined via Eq. (2.36) and  $\nu$  is the fluid viscosity. Sometimes, the value of hydraulic conductivity for a studied system is given. Then, the permeability tensor can be calculated as  $\kappa = K \frac{\nu}{\rho_f g}$ . Here, K is the tensor of hydraulic conductivity.  $\rho_f$  is the density of the fluid phase, and  $g = || \mathbf{g} ||$  is the magnitude of the gravity vector.

$$\boldsymbol{\kappa} := \begin{cases} \kappa(\phi) \cdot \begin{bmatrix} \kappa^{xx} & \kappa^{xy} & \kappa^{xz} \\ \kappa^{yx} & \kappa^{yy} & \kappa^{yz} \\ \kappa^{zx} & \kappa^{zy} & \kappa^{zz} \end{bmatrix} & \text{for 3D,} \\ \\ \kappa(\phi) \cdot \begin{bmatrix} \kappa^{xx} & \kappa^{xy} \\ \kappa^{yx} & \kappa^{yy} \end{bmatrix} & \text{for 2D,} \\ \\ \kappa(\phi) \cdot \kappa & \text{for 1D.} \end{cases}$$

$$(2.36)$$

The terms  $\kappa^{xx}$ ,  $\kappa^{yy}$ , and  $\kappa^{zz}$  represent the components of permeability matrix in the x-, y-, and z- directions, respectively.  $\kappa(\phi)$  is a multiplier used to update the permeability tensor  $\kappa$  when the porosity  $\phi$  is altered. This relationship is defined in Eq. (2.31). Note that, in this study, the two-phase mixture is assumed to be isotropic, which leads to the permeability tensor being reduced to a scalar value. For the effective stress of the solid matrix, we introduce a general rate form of the constitutive relation. In Section 2.5, each constitutive model is embedded for implementation.

$$\dot{\boldsymbol{\sigma}}' = \mathbb{C}^e : \dot{\boldsymbol{\epsilon}},\tag{2.37}$$

$$\boldsymbol{\epsilon} = \nabla^{sys} \boldsymbol{u} = \frac{1}{2} (\nabla \boldsymbol{u} + \nabla \boldsymbol{u}^T), \qquad (2.38)$$

where  $\mathbb{C}^e$  is the fourth-order tensor of elastic modulus, and  $\epsilon$  is the strain measure under the assumption of small strains. The operator  $\nabla^{sys}$  denotes the symmetric gradient of displacement.

To complete the problem, the boundary and initial conditions of this system are given below. The domain  $\Omega$  is occupied by the mixture with boundaries  $\Gamma$ . These boundaries are distinguished into different fields (such as fluid, solid, and chemical concentration in our system) and are classified into essential and natural boundary conditions. Here, we define the boundaries of our problem as follows:

 $\begin{array}{l} \Gamma_u \longrightarrow {\rm solid\ displacement\ boundary} \\ \Gamma_t \longrightarrow {\rm solid\ traction\ boundary} \\ \Gamma_p \longrightarrow {\rm fluid\ pressure\ boundary} \\ \Gamma_q \longrightarrow {\rm fluid\ flux\ boundary} \\ \Gamma_{c_i} \longrightarrow {\rm the\ specific\ chemical\ concentration\ boundary} \\ \Gamma_{q_{c_i}} \longrightarrow {\rm chemical\ concentration\ flux\ boundary}. \end{array}$ 

Some basic laws restrict the relationships between the decomposed boundaries. The first restriction is that the boundary  $\Gamma$  of a domain  $\Omega$  is a combination of decomposed boundaries for all sub-boundaries of the physical fields. The second restriction is that no overlap is allowed between decomposed boundaries for all sub-boundaries of the physical fields.

$$\Gamma = \Gamma_u \cup \Gamma_t = \Gamma_p \cup \Gamma_q = \Gamma_{c_i} \cup \Gamma_{q_{c_i}}, \qquad (2.39)$$

$$\Gamma_u \cap \Gamma_t = \Gamma_p \cap \Gamma_q = \Gamma_{c_i} \cap \Gamma_{q_{c_i}} = \emptyset.$$
(2.40)

In this case, the specified boundary conditions are given as:

- Specified displacement on  $\Gamma_u \longrightarrow \boldsymbol{u} = \bar{\boldsymbol{u}}$  (2.41)
- Specified traction on  $\Gamma_t \longrightarrow \mathbf{n} \cdot \boldsymbol{\sigma}' = \bar{t}$  (2.42)
- Specified pressure on  $\Gamma_p \longrightarrow p = \bar{p}$  (2.43)

- Specified flux on  $\Gamma_q \longrightarrow -\boldsymbol{n} \cdot \boldsymbol{\tilde{v}} = \bar{q}$  (2.44)
- Specified chemical concentration on  $\Gamma_{c_i} \longrightarrow c_i = \bar{c_i}$  (2.45)
- Specified chemical concentration flux on  $\Gamma_{q_{c_i}} \longrightarrow -\mathbf{n} \cdot \tilde{\mathbf{v}}_{c_i} = \bar{q}_{c_i}$  (2.46)

The initial conditions are set at time t = 0 as  $u_0$ ,  $p_0$ , and  $c_{i,0}$ . Note again that  $c_{i,0}$  denotes the initial concentration of the chemical species *i*.

#### 2.3.2 Variational formulation

To implement the finite element scheme to solve a problem, we introduce the variational form that corresponds to the equal-order displacement-liquid water pressure-chemical concentration finite element implementation. First, the weak form of the boundary value problem is defined. The three solution spaces for the three trial functions are defined as:

$$S_u = \{ \boldsymbol{u} : \Omega \to \mathbb{R}^3 | \boldsymbol{u} \in [H^1]^3, \boldsymbol{u} = \bar{\boldsymbol{u}} \text{ on } \Gamma_u \},$$
(2.47)

$$S_p = \{ p : \Omega \to \mathbb{R} \mid p \in H^1, p = \bar{p} \text{ on } \Gamma_p \},$$
(2.48)

$$S_{c_i} = \{c_i : \Omega \to \mathbb{R} \mid c_i \in H^1, \ c_i = \bar{c_i} \text{ on } \Gamma_{c_i}\},\tag{2.49}$$

Here,  $H^1$  denotes a Sobolev space of degree one. At the same time, the corresponding spaces of the weighting functions are defined on the essential boundaries as follows:

$$V_u = \{ \boldsymbol{\eta} : \Omega \to \mathbb{R}^3 | \boldsymbol{\eta} \in [H^1]^3, \boldsymbol{\eta} = \boldsymbol{0} \text{ on } \Gamma_u \},$$
(2.50)

$$V_p = \{\theta : \Omega \to \mathbb{R} \mid \theta \in H^1, \theta = 0 \text{ on } \Gamma_p\},$$
(2.51)

$$V_{c_i} = \{ \psi : \Omega \to \mathbb{R} \mid \psi \in H^1, \psi = 0 \text{ on } \Gamma_{c_i} \}.$$
(2.52)

In this case, the weak form of the problem now can find solutions  $\{u, p\} \in S_u \times S_p$  such that for all  $\{\eta, \theta\} \in V_u \times V_p$ . As for the chemical concentration, solutions also can be found  $\{c_i\} \in S_{c_i}$  such that for all  $\{\psi\} \in V_{c_i}$ . The reason for separating the solution of chemical concentration is that the staggered solving scheme is employed here. A detailed explanation of the solution strategy is provided in Section 2.4. Consequently, the weighted residual statement of the balance of linear momentum, the balance of mass, and the balance of chemical concentration are as follows.

$$G(\boldsymbol{u}, p, \boldsymbol{\eta}) = H(\boldsymbol{u}, p, \theta) = L(c_i, \psi) = 0, \qquad (2.53)$$

where  $G: S_u \times S_p \times V_u \to \mathbb{R}$  is the weak statement of the balance of the linear momentum. The derivation of G is as:

$$G(\boldsymbol{u}, p, \boldsymbol{\eta}) = -\int_{\Omega} \nabla^{sys} \boldsymbol{\eta} : \sigma' dV + \int_{\Omega} p \nabla \cdot \boldsymbol{\eta} dV + \int_{\Omega} \boldsymbol{\eta} \cdot \rho \boldsymbol{g} dV - \int_{\Gamma_t} \boldsymbol{\eta} \cdot \bar{\boldsymbol{t}} d\Gamma, \qquad (2.54)$$

where  $H: S_u \times S_p \times V_p \to \mathbb{R}$  is the weak statement of the balance of the mass. The derivation of H is as:

$$H(\boldsymbol{u}, p, \theta) = \int_{\Omega} \theta \nabla \cdot \dot{\boldsymbol{u}} dV + \int_{\Omega} \nabla \theta \cdot \frac{\kappa}{\nu} \nabla p dV - \int_{\Omega} \nabla \theta \cdot \frac{\kappa}{\nu} \rho_{w} \boldsymbol{g} dV - \int_{\Gamma_{q}} \theta \bar{q} d\Gamma, \quad (2.55)$$

where  $L: S_{c_i} \to \mathbb{R}$  is the weak statement of the balance of the chemical concentration. Lastly, the derivation of L is as:

$$L(c_{i},\psi) = \int_{\Omega} \psi \dot{c}_{i} dV - \int_{\Omega} \nabla \psi (\tilde{\boldsymbol{v}} \cdot \phi c_{i}) dV + \int_{\Omega} \nabla \psi \cdot (D_{i} \nabla c_{i}) dV - \int_{\Omega} \psi (S_{si} + S_{Ri}) dV - \int_{\Gamma_{qc_{i}}} \psi \bar{q}_{ci} d\Gamma.$$

$$(2.56)$$

We note that stabilized formulation for the mixed finite element with primary variables of solid displacement and pore pressure adopted for a fully coupled hydro-mechanical system. Please refer to the solution strategy for a coupled chemo-mechanical system of fluid infiltrating porous media in Section 2.4. The interpolated pore pressure is known to suffer from spurious oscillation in the undrained condition if solid displacement and pore pressure are spanned by the same basis function (Brezzi and Bathe, 1990; Murad and Loula, 1994; Schrefler et al., 1999). The reason for this problem is the lack of the inf-sup condition (White and Borja, 2008; Sun et al., 2013). As a result, either a Ladyzhenskaya-Babuska-Brezzi (LBB)-stable finite element pair or a stabilized formulation that allows for a broader range of stable combinations must be employed (Pastor et al., 2000; Truty and Zimmermann, 2006; White and Borja, 2008). The stabilized formulation proposed by White and Borja (2008) is adopted in this study, which allows for equal-order linear interpolation of the displacement and pressure fields while maintaining optimal convergence.

#### 2.3.3 Consistent linearization

We employ an implicit time integration method to solve the equations of the system. Therefore, an approximation or exact expression of the consistent tangent of the corresponding fields should be given and then be updated in an incremental format. Derivation of consistent linearization for the weak form Eqs.  $(2.54) \sim (2.56)$  is according to the variational formulation of displacement, pore pressure, and chemical concentration. The chemical concentration is only influenced by the velocity (treated as an invariant value in the same time step) induced by changes in pore pressure. The split algorithm is employed to deal with the couple's relations between the UP system and chemical concentration. Thus, when we solve transport equations of the chemical species, the solutions of the displacement and the pore pressure are frozen simultaneously.

For the linear momentum balance equation:

$$\Delta G(\boldsymbol{u}, p, \boldsymbol{\eta}) = -\int_{\Omega} \nabla^{sys} \boldsymbol{\eta} : \mathbb{C} : \nabla^{sys} (\Delta \boldsymbol{u}) dV + \int_{\Omega} \Delta p \cdot \nabla \cdot \boldsymbol{\eta} dV, \qquad (2.57)$$

where  $\mathbb{C} = \frac{\partial \sigma'}{\partial \epsilon}$ , which is the fourth-order tensor of tangent modulus. For the mass balance equation:

$$\Delta H(\boldsymbol{u}, p, \theta) = \int_{\Omega} \theta \cdot \nabla \cdot \frac{\Delta \boldsymbol{u}}{\Delta t} dV + \int_{\Omega} \nabla \theta \cdot \frac{\kappa}{\nu} \cdot \nabla(\Delta p) dV.$$
(2.58)

Here, we assume that saturated hydraulic permeability, fluid density, and fluid viscosity are not influenced by pressure. For the chemical concentration equilibrium equations:

$$\Delta L(c_i,\psi) = \int_{\Omega} \psi \cdot \phi \frac{\Delta c_i}{\Delta t} dV - \int_{\Omega} \nabla \psi \nabla \cdot \tilde{F}_i(\Delta c_i) dV + \int_{\Omega} \nabla \psi \cdot (D_i) \nabla (\Delta c_i) dV. \quad (2.59)$$

For the advection transport problem with high accuracy, Taylor-Galerkin algorithm (Donea, 1984; Löhner et al., 1984) is introduced in our study, which is widely applied to both fluid dynamics and solid mechanics (Peraire, 1986; Mabssout and Pastor, 2003). So we define a concentration flux  $\tilde{F}_i = \tilde{v}c_i$ , in which the Taylor-Galerkin method is described in Appendix A.1.

#### 2.3.3.1 Discretization in time

As mentioned in the preceding section, the implicit time integration method is employed to solve the system for the transient boundary value problems. Accordingly, the weak form of the residual statement, Eq. (2.53) must be discretized in time. The backward Euler scheme is adopted to discretize the weighted residual equation. The subscripts nand n + 1 denote temporally discrete quantities. Thus, the weighted-residual formula then can be arranged as:

$$\hat{G}(\boldsymbol{u}_{n+1}, p_{n+1}, \boldsymbol{\eta}) = \hat{H}(\boldsymbol{u}_{n+1}, p_{n+1}, \theta) = \hat{L}(c_{i,n+1}, \psi) = 0, \qquad (2.60)$$

where the weak statement of the balance of the linear momentum becomes:

$$\hat{G}(\boldsymbol{u}_{n+1}, p_{n+1}, \boldsymbol{\eta}) = -\int_{\Omega} \nabla^{sys} \boldsymbol{\eta} : \boldsymbol{\sigma}'_{n+1} dV + \int_{\Omega} p_{n+1} \nabla \cdot \boldsymbol{\eta} dV + \int_{\Omega} \boldsymbol{\eta} \cdot \rho \boldsymbol{g} dV - \int_{\Gamma_t} \boldsymbol{\eta} \cdot \bar{\boldsymbol{t}}_{n+1} d\Gamma,$$
(2.61)

with the weak statement of the balance of the mass being:

$$\hat{H}(\boldsymbol{u}_{n+1}, p_{n+1}, \theta) = \int_{\Omega} \theta \nabla \cdot \left(\frac{\boldsymbol{u}_{n+1} - \boldsymbol{u}_n}{\Delta t}\right) dV + \int_{\Omega} \nabla \theta \cdot \frac{\kappa}{\nu} \nabla p_{n+1} dV - \int_{\Omega} \nabla \theta \cdot \frac{\kappa}{\nu} \rho_w \boldsymbol{g} dV - \int_{\Gamma_q} \theta \bar{q}_{n+1} d\Gamma,$$
(2.62)

And the weak statement of the balance of the chemical concentration is:

$$\hat{L}(c_{i,n+1},\psi) = \int_{\Omega} \psi \phi \left(\frac{c_{i,n+1} - c_{i,n}}{\Delta t}\right) dV - \int_{\Omega} \nabla \psi \cdot (\tilde{F}_{i,n+\frac{1}{2}}) dV + \int_{\Omega} \nabla \psi \cdot (D_i) \nabla c_{i,n+1} dV - \int_{\Omega} \psi (S_{si} + S_{Ri})_{n+1} dV - \int_{\Gamma_{qc_i}} \psi \bar{q}_{c_{i,n+1}} d\Gamma.$$
(2.63)

#### 2.3.3.2 Discretization in space

For the discretization of the domain  $\Omega$ , we introduce the standard manner to define the shape functions for the weighting functions and unknowns. The finite element interpolations are linear in the discrete trial space  $\{S_u^h \times S_p^h\}$ ,  $S_{c_i}^h$ , and the weighting space  $\{V_u^h \times V_p^h\}$ ,  $V_{c_i}^h$ . Therefore, the fully discretized variational statement of the problem can be described as follows:

Find 
$$\{\mathbf{u}_{n+1}^h, p_{n+1}^h\} \in S_u^h \times S_p^h$$
 such that for all  $\{\mathbf{J}^h, \theta^h\} \in V_u^h \times V_p^h$ ,

Given 
$$\{c_{i,n+1}^h\} \in S_{c_i}^h$$
, find for all  $\{\psi^h\} \in V_{c_i}^h$ .

Therefore, the approximations are described as follows:

Unknowns:

displacement field 
$$\longrightarrow \boldsymbol{u}^h = \sum_{a=1}^n N_a \boldsymbol{u}_a$$
 (2.64)

fluid pressure field 
$$\longrightarrow p^h = \sum_{a=1}^h N_a p_a$$
 (2.65)

chemical concentration field 
$$\longrightarrow c_i^h = \sum_{a=1}^h N_a c_{i,a}$$
 (2.66)

Weighting functions:

displacement field 
$$\longrightarrow \boldsymbol{\eta}^h = \sum_{a=1}^n N_a \boldsymbol{\eta}_a$$
 (2.67)

fluid pressure field 
$$\longrightarrow \theta^h = \sum_{a=1}^h N_a \theta_a$$
 (2.68)

chemical concentration field 
$$\longrightarrow \psi^h = \sum_{a=1}^h N_a \psi_a$$
 (2.69)

Here, the superscript h denotes spatially discrete quantities.  $N_a$  is the shape function matrix,  $\boldsymbol{u}_a$ ,  $p_a$ , and  $c_{i,a}$  are nodal values of displacement, fluid pressure, and chemical concentration.  $\boldsymbol{\eta}_a$ ,  $\theta_a$ , and  $\psi_a$  are the corresponding nodal values of the weighting functions. The parameter n denotes the node number. Then, we substitute Eqs.  $(2.64)\sim(2.69)$  into Eq. (2.60). Using the standard Newton-Raphson iteration approach, we take  $\hat{G}$ ,  $\hat{H}$ , and  $\hat{L}$  as residuals of the fully discretized system of this study. The jacobian system used in Newton's iteration has the following format. We have a two-by-two block for the UP system and a one-by-one for the chemical concentration system.

$$\begin{bmatrix} \mathbf{A} & \mathbf{B}_{1} \\ \mathbf{B}_{2} & \mathbf{C} \end{bmatrix} \begin{bmatrix} \Delta u \\ \Delta p \end{bmatrix} = - \begin{bmatrix} \mathbf{R}_{mom.} \\ \mathbf{R}_{mas.} \end{bmatrix}$$
(2.70)

$$[M]\Delta c_i = -R_{i,con.} \tag{2.71}$$

Here,  $\Delta u$ ,  $\Delta p$ , and  $\Delta c$  are the nodal increments for displacement, fluid pressure, and chemical concentration over the given time interval. The right-hand side of the matrix are residuals, which are taken from  $\hat{G}$ ,  $\hat{H}$ , and  $\hat{L}$  Eqs. (2.61)~(2.63). We also list the block elements of the Jacobian system below.

Here, we note that the displacement, pressure, and chemical concentration fields are approximated as:

$$\boldsymbol{u}^{h} = \boldsymbol{N}^{\boldsymbol{u}}\boldsymbol{d}, \ p^{h} = \boldsymbol{N}^{\boldsymbol{p}}p, \ c^{h}_{i} = \boldsymbol{N}^{\boldsymbol{c}}c_{i},$$
 (2.72)

where the superscript h denotes spatial discretization same as previously defined,  $N^u$ ,  $N^p$ , and  $N^c$  are shape function matrices for displacement, fluid pressure and chemical concentration, d, p and  $c_i$  are nodal vectors corresponding to these fields. Then, the standard Galerkin approximations for the weighting functions are described as  $(a, \bar{a}, and \tilde{a} are arbitrary weights)$ :

$$\boldsymbol{\eta}^{h} = \boldsymbol{N}^{\boldsymbol{u}}\boldsymbol{a}, \ \boldsymbol{\theta}^{h} = \boldsymbol{N}^{\boldsymbol{p}}\bar{\boldsymbol{a}}, \ \psi^{h} = \boldsymbol{N}^{\boldsymbol{c}}\tilde{\boldsymbol{a}}.$$
 (2.73)

In this way, the block element of the Jacobian matrix can be expressed as:

$$\boldsymbol{A} = -\int_{\Omega} (\nabla^{sys} \boldsymbol{N}^{\boldsymbol{u}})^T : \mathbb{C} : (\nabla^{sys} \boldsymbol{N}^{\boldsymbol{u}}) dV$$
(2.74)

$$\boldsymbol{B}_{1} = \int_{\Omega} (\nabla \boldsymbol{N}^{\boldsymbol{u}})^{T} \boldsymbol{N}^{\boldsymbol{p}} dV \tag{2.75}$$

$$\boldsymbol{B_2} = \int_{\Omega} (\boldsymbol{N^p})^T (\frac{1}{\Delta t}) \nabla \boldsymbol{N^u} dV$$
(2.76)

$$\boldsymbol{C} = \int_{\Omega} (\nabla \boldsymbol{N}^{\boldsymbol{p}})^T (\frac{\kappa}{\nu}) \nabla \boldsymbol{N}^{\boldsymbol{p}} dV$$
(2.77)

$$\boldsymbol{M} = \int_{\Omega} (\boldsymbol{N}^{\boldsymbol{c}})^{T} (\frac{\phi}{\Delta t}) \boldsymbol{N}^{\boldsymbol{c}} + (\nabla \boldsymbol{N}^{\boldsymbol{c}})^{T} (\boldsymbol{D}_{\boldsymbol{i}}) \nabla \boldsymbol{N}^{\boldsymbol{c}} + (\nabla \boldsymbol{N}^{\boldsymbol{c}})^{T} (\tilde{\boldsymbol{F}}_{\boldsymbol{i}}) \boldsymbol{N}^{\boldsymbol{c}} dV, \qquad (2.78)$$

where  $\tilde{F}_i = \nabla \cdot F_i^{n+\frac{1}{2}}$  is based on two-step Taylor-Galerkin algorithm to expand in time, and use flux to give the time derivative at time  $n + \frac{1}{2}$ . The detailed derivations are given in Appendix A.1.

#### 2.4 Coupling of geochemistry and mechanical behavior

# 2.4.1 Combined operator-splitting and sequential iteration solution strategy

In this study, the operator-splitting scheme is used to solve the coupled system Eqs.  $(2.32)\sim(2.34)$ , while the sequential iteration approach is employed to solve fluid transport and geochemistry problems. The displacement d and pore pressure p system is solved using the linear solver in the first stage, while the chemical concentration  $c_i$  is held
fixed. In the second stage, displacement and pore pressure are fixed with the updated values from the first stage. Before solving the transport equation, the intra-aqueous reactions and kinetics are solved iteratively at the local Newton iteration of the transport equation using the iterative geochemistry solver. At the same time, the porosity and permeability parameters are also updated using the local equilibrium results of the above geochemistry. Finally, the chemical species transport is solved using the linear solver while the initial concentration of chemical species for each iteration corresponds to the result of the iterative geochemistry solver. We note that all local iterations occur at the Gauss points of each element. The key process is as follows:

$$\begin{bmatrix} \boldsymbol{d}_{n} \\ \boldsymbol{p}_{n} \\ \boldsymbol{c}_{i_{n}} \end{bmatrix} \underbrace{\stackrel{\hat{G}=0, \ \hat{H}=0}{\Delta c_{i}=0}}_{Linear \ solver} \begin{bmatrix} \boldsymbol{d}_{n+1} \\ \boldsymbol{p}_{n+1} \\ \boldsymbol{c}_{i_{n}} \end{bmatrix}} \underbrace{\boldsymbol{\Delta d}_{=0, \ \Delta p=0}}_{Linear \ solver} \begin{bmatrix} \boldsymbol{d}_{n+1} \\ \boldsymbol{p}_{n+1} \\ \boldsymbol{c}_{i_{n}} \end{bmatrix}} \underbrace{\stackrel{\hat{L}=0}{\boldsymbol{\Delta d}_{=0, \ \Delta p=0}}}_{Linear \ solver} \begin{bmatrix} \boldsymbol{d}_{n+1} \\ \boldsymbol{p}_{n+1} \\ \boldsymbol{c}_{i_{n+1}} \end{bmatrix}}_{Linear \ solver} \tag{2.79}$$

#### 2.4.2 Coupling scheme and algorithm

The operator-split solution strategy is illustrated through the flow chart shown in Figure 2.1, as follows: Knowing Darcy's velocity and the concentration values of each chemical species for each integration node at time n, the transport solver computes the new concentration values at time n + 1. During the setup and assembly of the transport equation matrix, the intra-aqueous equilibrium calculation determines the redistribution of concentration triggered by the diffusion-advection transport (which is in non-equilibrium) for each Newton iteration step. At the same time, the kinetic equilibrium calculation determines the kinetic reaction between the solid-fluid and fluid component-component. Finally, we obtain updated concentration values for all chemical species, which are in a local chemical equilibrium state.

The numerical model is implemented using Geocentric, a massively parallel finite element code for geomechanics, built on the open-source finite element library deal.II (Bangerth et al., 2007, 2013), interfaced with the p4est mesh handling library (Burstedde et al., 2011), and the Trilinos project (Heroux and Willenbring, 2012). This code has been used in previous studies including multiphysics problems (e.g., (White and Borja, 2008, 2011; White et al., 2016; Na and Sun, 2017; Na et al., 2017)).

Geocentric computes the mechanical response in terms of elastic/elastoplastic strains



FIGURE 2.1: Flow chart for coupling the geochemistry reactions with the mechanical behavior.

and also the new Darcy's velocity induced by changes in pore pressure. Whenever we calculate a new mechanical response the chemical saturation index is employed to update the new hydraulic conductivity and porosity parameters.  $K_{eq_{calcite}}$  is the equilibrium constant of the calcite dissolutions which is only related to temperature.  $Q_{calcite}$  is from the concentration values relevant to the reactions of calcite at the equilibrium state. Details can be found in Eq. (2.26). The algorithm for the coupling is summarized in Table 2.4:

TABLE 2.4: Algorithm 2-1: Operator-splitting algorithm for chemomechanical coupling model

A 1 • 1 1 A	0 1	O 1 1.1.1	1 • 1	C	1 1	• 1	1.	1 1
Algorithm 1	2-1.	Operator-splitting	algorithm	tor	chemo-mech	anical	counting	model
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1: Initialize all input parameters:	
solid, fluid, chemical solution.	$\triangleright c_0$ must be given.
for each time step $t_n$ do	
Part 1: coupling solid and fluid mechanics	
for each iteration step $k_n$ do	
<b>2</b> : Setup, assemble, and solve $d_{n+1}$ , $p_{n+1}$ .	$\triangleright$ See Eqs. (2.74) ~(2.77), (2.70).
<b>3</b> : Update $\tilde{\boldsymbol{v}}_{n+1},  \tilde{\boldsymbol{v}}_{n+\frac{1}{2}}$ using $p_{n+1}$ .	$\triangleright$ See Eqs. (2.35),(A.8).
until $\delta d$ , $\delta p < \text{Tolerance}$ , end for	
Part 2: geochemistry process	
4: Initial intra-aqueous equilibrium calculation.	
1). Calculate $K_i$ , $\kappa_i$ , and $k_i$ .	$\triangleright$ See Table 2.1.
2). Calculate $\gamma_i$ and $I$ .	$\triangleright$ See Eqs. (2.17)~(2.19), Table 2.2.
3). Bisection method to find PH value.	$\triangleright$ See Eq. (2.25).
4). Update concentration values for all species.	$\triangleright$ See Eqs. (2.12)~(2.16) and (2.24).
5). Output calcite saturation index $\Omega = \frac{Q_{calcite}}{K_{eq_{calcite}}}$ .	$\triangleright$ See Eq. (2.26).
5: Update porosity and intrinsic permeability.	$\triangleright$ See Eqs. (2.28)~(2.31).
Part 3: Reactive fluid transport	
for each iteration step $k_n$ do	
6: Calculate intra-aqueous equilibrium	
again following Step 4. $1$ )~5).	
<b>7</b> : Setup, assemble and solve $c_{i,n+1}$ .	$\triangleright$ See Eqs. (2.71) and (2.78).
until $\delta c_i < \text{Tolerance}$ , end for	
8: Output	
9: end for	

Remark 1. In Table 2.4, Algorithm 2-1, the initial intra-aqueous equilibrium calculation

establishes an equilibrium state before the reactive transport fluid flows. Thus, Step 4 is performed only once per time step. It is worth noting that, inside the reactive fluid transport, we calculate the geochemistry process at every iteration, which follows the same procedure as Step 4. However, the time for the calculation of the geochemistry process is maintained the same during the iteration steps of fluid transport.

### 2.5 Numerical examples

Three numerical examples are selected to test the performance and applicability of the proposed framework for coupled hydro-mechanical-chemical processes in saturated porous media, including chemical reaction, solid deformation, pore pressure diffusion, and porosity changes. Since calcite dissolution/precipitation is a very slow physical process, a large time step may trigger unstable computations and chemical reactions far from equilibrium. Specifically, large time steps may cause excessive calcite dissolution/precipitation, leading the geochemistry solver to non-convergence. Therefore, in our simulation work, we select the time step based on the condition that the calcite dissolution/precipitation concentration within the time step is of the same order of magnitude as the initial concentration values, that is,  $t \leq \frac{c_{i,0}}{\gamma_{\beta}}$ . We assume that calcite maintains a constant reaction rate within each time step.

First, we investigate two examples that simulate the coupled effects of fluid advectiondiffusion and solid deformation associated with chemical reactions. The advectiondiffusion of chemical concentration is driven by the pore pressure induced by solid deformation. Analytical solutions for the one-dimensional fluid advection-diffusion problems proposed by Price et al. (1968) are employed to compare with the computational results of the proposed model. For the chemical reaction, we conduct benchmark simulations to validate the precision of the geochemistry solver for the chemical reactions calculation. The experimental data from Dreybrodt (1999) and Nghiem et al. (2004) are used for comparison. Then, a showcase for classical Terzaghi's two-dimensional consolidation is presented, where the consolidation process is influenced by the coupled displacement-pore pressure-transport-reaction effects. Finally, to further illustrate the porosity evolution with time and chemical reaction progress, we present a special case to show the porosity changes due to calcite dissolution/precipitation.

### 2.5.1 Verification example: diffusion and advection-diffusion transport

The first example compares the results of the proposed model to analytical solutions of one-dimensional pure diffusion transport. Schematic diagrams of the geometry and boundary conditions are shown in Figure 2.2. We set the same material parameters and initial conditions for both computational and analytical solutions as follows: porosity  $\phi = 0.8$ , diffusivity  $D = 1.152 \times 10^{-7} m^2 / min$ , and source/sink terms  $S_R = S_s = 0$ . The size of the specimen is  $0.1 \ m \times 0.05 \ m$ , and both the top and bottom are set to drainage conditions. The top of the specimen is a free end, while the bottom is a fixed end. The initial concentration inside the specimen is  $c_0 = 0 \ molality$ , and a constant concentration of  $\bar{c} = 1.0 \ molality$  is applied on the top surface. A structured mesh with an element size of  $h = 0.002 \ m$  is designed with a time step of  $\Delta t = 1 \ min$ .

The second comparison is conducted for one-dimensional advection-diffusion transport, as shown in Figure 2.3. We follow the same configurations as in the first example, but different material parameters and boundary conditions are considered: (1) material parameters: fluid density  $\rho_f = 1.0 \ kg/m^3$ , fluid viscosity  $\nu = 1.667 \times 10^{-6} \ kPa \cdot min$ , intrinsic permeability  $\kappa = 1.0 \times 10^{-12} m^2$ ; and (2) the top boundary for pore pressure is set as a constant flux  $\bar{q} = -50 \ kPa/m$ .

Figures 2.2b and 2.3b depict the concentration profiles at times t = 200, 400, 600, and 800 min, respectively. In Figures 2.2b and 2.3b, the blue solid lines represent the analytical solutions (Price et al., 1968), while the red dashed lines are the numerical results of the proposed model. As time increases, the concentration fronts migrate from the top to the bottom of the specimen. The numerical results show good agreement with the analytical results for both pure diffusion and advection-diffusion problems. As mentioned in Section 2.3, we employ the Taylor-Galerkin scheme to discretize the fluid advection-diffusion equation for advection-dominated flows in the finite element analysis. Figure 2.3b shows the accuracy of the numerical solutions corresponding to the advection-dominated problems. In short, the verification example demonstrates the capability of the proposed model to capture both fluid diffusion and advection-diffusion problems.



FIGURE 2.2: (a) Schematic of geometric and boundary conditions for pure diffusion problem; (b) time-dependent concentration distribution along the height of the specimen ( $t = 200 \ min$ , 400 min, 600 min, and 800 min).



FIGURE 2.3: (a) Schematic of geometric and boundary conditions for diffusion and advection problem; (b) time-dependent concentration distribution along the height of the specimen (t = 200 min, 400 min, 600 min, and 800 min).

## 2.5.2 Verification example: chemical equilibrium with and without calcite dissolution

In this section, we verify the accuracy of the geochemistry solver. We distinguish the chemical reaction systems into two different conditions: (1) a known initial non-equilibrium chemical system without calcite dissolution, and (2) a known initial non-equilibrium chemical system with calcite dissolution. In other words, Condition (2) considers the interactions between mineral and fluid, while Condition (1) does not.

For Condition (1), the initial configurations for the non-equilibrium chemical systems are given in Table 2.5. Here, we conduct 7 cases to calculate the final concentration values of chemical species when the non-equilibrium systems reach equilibrium. As seen in Section 2.2, the initial concentration of  $Ca^{2+}$  and partial pressure  $p_{CO_2}$  determine the final equilibrium state in the current model. Thus, we only set different initial concentrations of  $Ca^{2+}$  and partial pressure  $p_{CO_2}$ , and calculate the final concentration values for the remaining chemical species in the system.

Case number	$Ca^{2+}$ concentration	$p_{\rm CO_2}$
Case 1	$2.0 \times 10^{-4} molality$	$0.008 \ atm$
Case 2	$4.0 \times 10^{-4} molality$	$0.008 \ atm$
Case 3	$6.0 \times 10^{-4} molality$	$0.008 \ atm$
Case 4	$8.0 \times 10^{-4} \ molality$	$0.008 \ atm$
Case 5	$1.0 \times 10^{-3} molality$	$0.008 \ atm$
Case 6	$1.2 \times 10^{-3} molality$	$0.008 \ atm$
Case 7	$1.4 \times 10^{-3} molality$	$0.008 \ atm$

TABLE 2.5: Initial configurations for the non-equilibrium chemical systems

We verify the concentration values for all species in our chemical system when it reaches an equilibrium state. Dreybrodt (1999) conducted systematic research on the chemistry of the H<sub>2</sub>O-CO<sub>2</sub>-CaCO<sub>3</sub> system and reported some reliable experimental data, which is used for comparison in this example. In Figures 2.4 and 2.5, circles represent the experimental data, while solid lines represent the numerical calculation results. We plot the curves and circles in two figures according to the order of magnitude. Figure 2.4 shows the comparison results for the chemical species Ca<sup>2+</sup>, H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, CO<sub>2</sub><sup>0</sup>, and HCO<sub>3</sub><sup>-</sup>. The line of H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> concentration is expressed as the total amount of CO<sub>2</sub><sup>0</sup> (H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> =  $CO_2^0 + H_2CO_3^0$ ), which shows a parallel tendency to the amount of CO<sub>2</sub><sup>0</sup>. For every case point, the numerical calculations show good agreement with the experimental data. Figure 2.5 shows the comparison results for the remaining chemical species ( $H^+$ ,  $OH^-$ , and  $CO_3^{2-}$ ).In contrast, the concentrations of these species are minor but play important roles in chemical equilibrium. The concentration of  $CO_3^{2-}$  is observed to be slightly lower than the experimental data. Additionally, to further understand the final equilibrium values of different species under different concentration configurations, we make a solid line across all those seven cases' data, shown as solid lines in Figures 2.4 to 2.5. As mentioned at the beginning of the numerical examples, the initial concentration values are vital for determining the simulation time step. Therefore, the results of this equilibrium state can help us select an appropriate time step for simulations.

Overall, for Situation (1), a known initial non-equilibrium chemical system without calcite dissolution, comparison results show that the geochemistry solver captures the chemical mechanisms accurately.



FIGURE 2.4: Seven Cases for concentration of  $Ca^{2+}$ ,  $H_2CO_3^*$ ,  $CO_2^0$ , and  $HCO_3^-$ .



FIGURE 2.5: Seven Cases for concentration of  $H^+$ ,  $CO_3^{2-}$ , and  $OH^-$ .

For Situation (2), the initial configuration for the non-equilibrium chemical system with calcite dissolution can be found in Appendix A.2. We consider the calcite dissolution process induced by the non-equilibrium state of the solution. Recall the definition of the saturation index in Eq. (2.26), which is the ratio  $(Q_{\beta}/K_{eq_{\beta}})$ . This ratio must be calculated to account for the interactions between the mineral and the solution. When  $Q_{\beta} \neq K_{eq_{\beta}}$ , there is a dynamic kinetic reaction rate driving calcite dissolution into the solution. Therefore, in the verification of Situation (2), we not only focus on the intra-aqueous equilibrium, like in Situation (1), but also consider the intra-aqueous equilibrium after the calcite dissolution.

Additional material parameters are adopted to calculate the quantity of Calcite dissolution into the solution. The rate constant in Eq. (2.26) is  $1.6 \times 10^{-9} mol/m^2/s$ . The activation energy is 41,870 J/mol, and the reactive surface area of the Calcite is  $8.8 m^2/m^3$ . This system contains 10 g of Calcite and 100 g of water. The environmental temperature is  $25^{\circ}C$  under a standard atmospheric pressure of 101.325 kPa.

We verify the concentration values for all species when calcite dissolution occurs in the system. Nghiem et al. (2004) validated their compositional simulator GEM-GHG using Geochemist's Workbench®(GWB) geochemistry software (Kestin et al., 1981). They presented the evolution of different components over time, which was highly consistent with the geochemistry calculations in GEM-GHG and GWB. In this validation, we select

the reliable data of Nghiem et al. (2004) to compare with our results (Figures 2.6 and 2.7).

In Figure 2.6, circles represent the simulation results of Nghiem et al. (2004), while solid lines represent the numerical results of the proposed model. The concentrations of  $CO_2(aq)$  and  $Ca^{2+}$  show consistent results, while  $HCO_3^-$  yields slightly higher values in the proposed model. One possible reason is that the effect of ion pairs is not considered in our model. However, in the work of Nghiem et al. (2004), all ion pairs, such as  $CaHCO_3^+$ , were considered. We also calculate the concentration of dissolved Calcite and depict it in the secondary coordinates of Figure 2.6. The solubility of Calcite increases over the first 50 days and then becomes constant, indicating that the whole solution (solid-fluid and intra-aqueous) reaches an equilibrium state.



FIGURE 2.6: Time-dependent reaction concentration of  $Ca^{2+}$ ,  $CO_2$ ,  $HCO_3^-$ , and calcite.

In Figure 2.7, the results of chemical species, including  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ , and  $\text{H}^+$ , are presented, showing relatively large discrepancies when compared with those of Nghiem et al. (2004). Discrepancies are also observed in Figure 2.6. Although the impacts of ion pairs are not considered in this study, Nghiem et al. (2004) considered the chemical reactions of the ion pairs, such as  $\text{CaHCO}_3^+$  and  $\text{CaCl}^+$ .

Combining the results of Figures 2.3 to 2.6, we conclude that  $Ca^{2+}$  is a key species in determining the final equilibrium state, and  $HCO_3^-$  is the key species in considering the effect of ion pairs. For additional analysis, we plot the chemical saturation index on the

secondary coordinates in Figure 2.7, illustrating the saturation state of calcium ions in the solution. The result shows that the chemical saturation index keeps increasing during the first 50 days and then oscillates around 1 after 50 days. This tendency is consistent with the theory of the transition from nonequilibrium to equilibrium of the whole chemical system, from undersaturated to saturated, and even a bit of supersaturation. We also conclude that mineral dissolution equilibrium determines the final equilibrium of the solid-fluid system. Otherwise, mineral reactions always disturb the intra-aqueous equilibrium.



FIGURE 2.7: Time-dependent reaction concentration of  $OH^-$ ,  $H^+$ , and  $CO_3^{2-}$ .

#### 2.5.3 Two-dimensional consolidation case

In this section, we showcase the capability of the proposed model to simulate the displacement-pore pressure-transport-chemical reaction inside a homogeneous soil specimen. The dimensions of the simulation domain are shown in Figure 2.8. The top surface, left side, and right are drainage boundaries.

To be consistent with the pore pressure, we set all of the chemical species to be 0 on the top surface. Both pore pressure and chemical concentrations are impermeable at the bottom of the boundary. The initial pore pressure and chemical concentrations are constant, which can be found in Table 2.6. To illustrate the diffusion of pore pressure, displacement, and evolution of porosity of the domain, we select points A, B, and C beneath the top surface to investigate the results.

Consolidation in soil refers to the process by which soil gradually reduces in volume under an applied load, primarily due to the expulsion of pore water. Therefore, the key aspect to address in the model is the consideration of pore water. Terzaghi's consolidation theory forms the foundation for understanding soil consolidation. It assumes one-dimensional deformation and flow, where soil consolidates in the vertical direction due to a vertical load. Extensions of Terzaghi's theory to two-dimensional (2D) or threedimensional (3D) consolidation models are used to simulate more complex conditions. When analyzing soil consolidation with the simultaneous effects of deformation and fluid flow, it involves coupled soil displacement and pore water flow. If mass exchange occurs between the solid and fluid phases, the hydraulic conductivity of the soil is influenced, which further affects the consolidation process.

In this section, the numerical example discusses the consolidation process of soil to comprehensively present the following scenarios:

- (1) Two-dimensional Terzaghi's consolidation;
- (2) Coupled displacement-pore pressure consolidation;
- (3) Coupled displacement-pore pressure and reactive flow consolidation.

A set of material properties used in the simulation, including the solid matrix, fluid, and chemical solution, is listed in Table 2.6. We first investigate the diffusion of pore water pressure by comparing scenarios (1), (2), and (3). Figure 2.9 compares the effects



FIGURE 2.8: Schematic of geometry, boundary, and initial conditions for the numerical test of Terzaghi's consolidation.

of the different scenarios up to 70 seconds. The figure depicts the dissipation of excess pore water pressure for each scenario. From the solid line in Figure 2.9, we observe that the pore water pressure decreases fastest in scenario (1), followed by scenarios (3) and (2). The two-dimensional consolidation theory follows a constant coefficient of consolidation. Pore pressure diffusion in scenario (1) is directly connected with soil volume compressibility. Scenario (2), however, places more emphasis on the mass balance of pore water and Terzaghi's effective stress theory, resulting in a different consolidation process performance.

In Figure 2.9, there appears to be no difference between scenarios (2) and (3) from 1 to 10 seconds. However, a clear difference emerges after 10 seconds and continues until all excess pore water is drained from the soil. This difference is triggered by the chemical reactions occurring within the void space, increasing porosity, which accelerates the diffusion of excess pore pressure. At the same time, the alteration in porosity is not immediate.

Parameter	Description [Unit]	Value				
Environmental conditions						
T	Temperature $[^{\circ}C]$	80				
$T_0$	Reference temperature $[^{\circ}C]$	25				
$p_0$	Reference pressure $[kPa]$	100				
Solid matrix						
$ ho_s$	Intrinsic solid mass density $[kg/m^3]$	2700.0				
V	Intrinsic volume of specimen $[m^3]$	$1.9625\times10^{-4}$				
w	calcite mass percentage [%]	0.08				
$\hat{A_0}$	Specific surface area of calcite $[m^2/m^3]$	$2.62\times 10^6$				
M	calcite molar weight $[kg/mol]$	$100.0869 \times 10^{-3}$				
$\phi_0$	Reference porosity [-]	0.23				
$\kappa_0$	Reference permeability $[m^2]$	$1.0 \times 10^{-13}$				
Fluid						
$ ho_f$	Intrinsic fluid mass density $[kg/m^3]$	1000.0				
$\nu$	Viscosity of fluid $[kPa \cdot s]$	$1.0 \times 10^{-6}$				
$D_{\rm CO_2}$	Diffusivity of $CO_2 [m^2/s]$	$1.785  imes 10^{-8}$				
$D_i$	Diffusivity of rest of ions $[m^2/s]$	$1.25 \times 10^{-8}$				
Chemical solution	· · · · ·					
$V_q$	Volume of gas $[m^3]$	0.0				
$V_{l}$	Volume of liquid $[m^3]$	100				
$\kappa_{eta}$	Reaction constant $[mol/m^2s]$	$1.6 \times 10^{-9}$				
$\dot{E_{eta}}$	Activation energy $[J/mol]$	41,870				

TABLE 2.6: Material parameters for the numerical classical Terzaghi's two-dimensional consolidation test

We now consider the vertical displacement of the soil. The results for scenarios (2)



FIGURE 2.9: Comparison of pore pressure diffusion between mechanical, hydro-mechanical coupling, and chemo-hydro-mechanical coupling.

and (3) are presented in Figure 2.10, which illustrates the vertical relative displacement occurring at four different locations within 100 seconds. Overall, the differences in displacement between the coupled hydro-mechanical consolidation and the coupled chemo-hydro-mechanical consolidation are not as obvious as the differences in diffusion of pore pressure. A more detailed comparison reveals that the vertical displacement behavior is consistent with the diffusion of pore pressure. As time progresses, the settlement induced by chemical reactions becomes more pronounced. We observe that all four locations are influenced by the chemical reactions. Below the surface, the entire domain undergoes chemical reactions involving both the chemical species in the liquid pore water and the mass exchange between these species and the solid mineral. Thus, compared to consolidation scenario (2), we can observe the additional settlement caused by the chemically induced effects in consolidation scenario (3).

Lastly, we depict the pore pressure dissipation contour and liquid solution streamlines in Figure 2.11. We observe fluid flowing in two dimensions, with the flow path evolving as pore pressure dissipates. In the initial dissipation phase, most fluid flows in the vertical direction. However, in the final dissipation phase, the fluid tends to flow laterally. Additionally, the fluid streamline distribution is non-uniform within the domain, a result of chemical degradation effects.

We validate our calculations predicting porosity changes by comparing them with



FIGURE 2.10: Comparison of vertical displacement between mechanical and chemo-mechanical coupling.



FIGURE 2.11: The effect of considering chemical reactions on chemohydro-mechanical coupled consolidation. Pore pressure distribution with fluid flow streamlines. (a) 1 s; (b) 20 s; (c) 70 s.

the results of dynamic three-dimensional pore-scale imaging of reactions in carbonate, following the homogeneous carbonate configuration of Menke et al. (2015). The merit of our model lies in its ability to extract information about  $Ca^{2+}$  to predict the dissolution of calcite and characterize porosity changes. Consequently, we compare the prediction results of our model with their image-measured data. The initial porosity is 0.18, and the initial absolute permeability is  $2.8 \times 10^{-11} m^2$ . We define the normalized porosity and permeability by referring to the initial values  $Normalized = \frac{Alternated}{Initial}$ . The results of 10 imaged-average porosity measurements are compared with our study. As shown in Figure 2.12, the results of CT images are consistent with our simulation results. The difference arises from the lack of characterization of the pore networks, such as pore radius shape, number of throats, and throat shape. It's worth noting that the formulation we use to calculate permeability underestimates the influence of porosity on permeability when the normalized porosity reaches 2.0. In general, we confirm that the coupled model of deformation, fluid transport, and reaction can achieve similar results to experiments on porosity alteration. We further focus on the near saturation levels of  $Ca^{2+}$  in the liquid solution. As shown in the validated benchmark results in Figure 2.7, the fluctuation of the saturation index in the system indicates mineral dissolution and precipitation. Therefore, we set a function, as shown in Figure 2.13, to demonstrate the fluctuation observed in the benchmark. We then observe the porosity response at four layers shown in diagram Figure 2.8 within 100 s. Figure 2.14 shows the porosity distribution contours at 10, 50, 90, and 100 seconds. From 10 to 50 seconds, we observe a precipitation phenomenon above surface A, while dissolution occurs below surface A with varying intensities. After 90 seconds, calcite dissolution occurs throughout the entire domain. This process is further evidenced by the curves in Figure 2.15, which display the porosity distribution of the top surface, surface A, surface B, surface C, and the bottom surface. The curves indicate that both precipitation and dissolution processes are occurring on the top surface, where porosity initially decreases and then increases. Surface A exhibits weak precipitation and also shows signs of dissolution. Surfaces B, C, and the bottom surface experience continuous dissolution, with the dissolution rate increasing correspondingly.



FIGURE 2.12: Verification of the normalized porosity and permeability alterations with time.



FIGURE 2.13: Assumptions on chemical saturation index evolution with time and vertical location.



FIGURE 2.14: Distribution of porosity under chemical reactions with time.



FIGURE 2.15: Porosity changes with time for the top surface, surface A, surface B, surface C, and the bottom surface.

### 2.6 Summary

We developed a computational framework to solve the coupled chemo-hydro-mechanical processes in saturated porous media by establishing local chemical equilibrium via the finite element method. The multi-component  $\rm CO_2-H_2O-CaCO_3$  the system was selected as a typical system representing major pore geochemistry occurring within fluid-infiltrating porous media. The framework for the geochemistry of reactive multi-component systems is scalable to incorporate different sets of chemical reactions by establishing local equilibrium for each chemical species. Additionally, this geochemistry framework can capture intra-aqueous chemical reactions occurring inside pores and kinetic rate-limiting chemical reactions occurring on the surface of reactive minerals.

We introduced an algorithm where multiple reactive transport equations are calculated in a standard finite element scheme without demanding significant computational cost, allowing for easy incorporation into existing hydro-mechanical or thermo-hydromechanical models for fluid infiltrating porous media. To better analyze coupled chemomechanical alterations in porous media, we introduced the saturation index to characterize the dissolution saturation of a mineral, describing the mass exchange process between reactive fluid and solid mineral. Finally, additional changes in porosity and permeability due to mass transfer were characterized using the Kozeny-Carman equation. This concept enables us to account for the mechanical responses associated with changes in material properties.

We verified the proposed framework by comparing the numerical results with analytical solutions and existing experimental data. Through a series of numerical examples, we demonstrated the potential applicability and accuracy of our model in capturing the coupled effects of pore geochemistry on deformable porous media. The computational framework established in this work integrates multiple mechanisms for reactive flow and geomechanics, comprehensively illustrating the impacts of chemical reactions on evaluating long-term stability in geotechnical engineering.

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### Chapter 3

## A reactive transport phase-field modeling approach for chemo-assisted cracking in saturated sandstone

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### A reactive transport phase-field modeling approach for chemo-assisted cracking in saturated sandstone

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### Abstract

Hydraulic fracturing and acidizing techniques are important approaches for deep energy recovery engineering. However, the details of the interactions and impacts between acid fluids and solid porous media remain inadequately modeled, necessitating further research in this domain. Building on this need, we present a novel approach for modeling the chemo-hydro-mechanical response in sandstone during fracture propagation, which is induced by the injection of acid fluids into a reservoir. Our comprehensive framework integrates various mechanisms, including acidified reactions in sandstone, reactive flow transport, pore pressure diffusion, solid deformation, mass exchange due to chemical reactions, and fracture propagation in poroelastic media, all within the framework of the phase field approach. To accurately capture the system's behavior, we derive its total potential energy, taking into account factors such as poroelasticity, fracture forces acting on the fracture sides, and crack dissipation, while also integrating the mechanicalchemical degradation function into the energy derivations. The progress of chemical degradation, which we treat as a damage parameter, is characterized by mass exchange, and this in turn manifests as changes in porosity. To quantify these mass exchanges, we have established a corresponding mass balance equation specifically for the minerals involved. These changes in porosity can be naturally and effectively described through

the volumetric relations among the minerals situated within the solid porous media. The proposed coupled framework is verified through multiple numerical examples. Initially, we validate our model using a classical unit-slit crack example for the solid phase and discuss the predominant influences of porosity alterations on the mechanical response of solid cracking. Following this, we verify the model by injecting water/acid and compare the results with analytical solutions. Finally, a chemical benchmark is employed to calibrate the chemical reaction model and simulate acid fluid injection scenarios.

**Keywords:** Phase-field approach, Chemo-mechanical coupling, Poroelastic, Mineral dissolution, Chemical damage.

### 3.1 Introduction

Sandstone acidizing is an important technology in the oil and gas recovery industry. The best-known acid combination is mud acid, constituted of hydrofluoric acid and hydrochloric acid (HF : HCl), which effectively enhances the porosity and permeability of the reservoir formation, as well as well productivity (Shafiq and Mahmud, 2017). However, energy recovery projects are experiencing increasingly complex production scenarios because new reservoirs are typically located in deeper and higher-temperature regions (Qun et al., 2019). As a result, the mud acid technique becomes more corrosive, easily forming precipitations, and reacts rapidly, leading to early acid consumption (Al-Harthy et al., 2008). Consequently, these challenges can decrease the effectiveness of reservoir acidizing.

One of the recent techniques combines the advantages of matrix acidizing technology and hydraulic fracturing technology to address such challenges. Hydraulic fracturing creates artificial fractures that serve as high-permeability pathways, allowing reactive fluids to travel further away from the well. As a result, changes in petrophysical properties occur over a larger area, significantly enhancing the effectiveness of matrix acidizing for enhanced oil recovery. Researchers have conducted a series of studies on the effects of sandstone acidizing on the efficiency of energy recovery. Gunawan et al. (2012) analyzed fracture-assisted sandstone acidizing to increase the efficiency in tight sandstone reservoirs. Zhao et al. (2022) conducted a study on the effectiveness of the three-stage acid fracturing technology in tight sandstone reservoirs with undeveloped natural fractures. However, unlike conventional hydraulic fracturing methods, the injection of acid fluids accelerates fluid-rock interactions. In other words, more reactions between acids and multiple minerals in both the fractures and matrix pores greatly impact fracture behavior in porous media (Schuler et al., 2020; Clavijo et al., 2022). Therefore, it is crucial to have a deep understanding of these acidizing reactions to investigate the coupled chemical-hydromechanical process in hydraulic fracturing and to effectively control fracture behavior through acid fluid injection in energy recovery processes.

The acidic environment in engineering scenarios, such as sandstone acidizing and  $CO_2$  geological sequestration, renders the reservoir susceptible to chemical reactions. Some laboratory experiments have studied the chemo-mechanical coupling effects (Castellanza and Nova, 2004; Ciantia and Hueckel, 2013; Ciantia et al., 2015; Kahlouche et al., 2021), highlighting the dissolution/precipitation of minerals as one of the primary mechanisms for such chemo-mechanical interactions.

There are generally four categories of mathematical models used to describe the dissolution/precipitation of minerals: the lumped-parameter model, two-parameter model, four-parameter model, and detailed chemistry model. The lumped-parameter model simplifies all reactive minerals into a single soluble species and does not consider the sequential reactions between the resulting compound of hydrofluoric acid and minerals. Notably, significant contributions to this field have been made by McCune et al. (1975); Fogler et al. (1976). The simplified model is commonly used to study acid-rock interactions and captures changes in porosity, but it is not precise enough to fully represent the complex reactions. As a result, the lumped-parameter model was further expanded by Hekim et al. (1982), and a new two-parameter model was developed. The two-parameter model differentiates minerals into two categories: slow-reacting minerals (such as quartz) and fast-reacting minerals (such as feldspar and clay). However, this model disregards secondary reactions associated with the intermediate product  $(H_2SiF_6)$ , as demonstrated by Da Motta et al. (1993); Al-Shaalan and Nasr-El-Din (2000), indicating its limited applicability in high-temperature conditions where fast-reacting minerals and silica gel precipitations are absent. Bryant (1991) expanded the two-parameter model into the four-parameter model, incorporating secondary reactions and silica gel precipitation. The accuracy of this model has been validated through several experimental investigations (Rodoplu et al., 2003; Li, 2004; Mahmoud et al., 2020). For instance, PhreeqcRM (Parkhurst and Wissmeier, 2015) is known to be one of the most robust simulators capable of capturing mineral reactions.

Numerous researchers have conducted studies to develop a unified field formulation to predict the multi-physical behavior of hydraulic fracturing in porous media, particularly concerning chemically coupled problems. Miehe et al. (2010a,b) introduced a thermodynamically consistent framework for phase-field models and investigated numerical implementations using multi-field finite element methods within this framework. Martínez-Pañeda et al. (2018) introduced a phase-field modeling framework for hydrogen-assisted cracking, successfully simulating coupled mechanical and hydrogen diffusion problems. This study supported the conclusion that phase-field methods for fracture are well-suited for addressing coupled chemo-mechanical problems. Building on the work of Martínez-Pañeda et al. (2018), Schuler et al. (2020) developed a framework to address fracture propagation in a chemically reactive environment. They introduced a representative system involving calcite dissolution resulting from  $CO_2$ , which is significant for  $CO_2$ sequestration. Clavijo et al. (2022) presented a coupled framework that considers the hydro-chemo-mechanical responses in rock formations experiencing fracture propagation in chemically active environments. They utilized the Phreeqc solver to analyze mass exchange in carbonate-rich sandstone. Xie et al. (2023) proposed a multi-stage reactivetransport simulation model that integrates multiple mineral reactions with the extended finite element method to simulate reactive flow in fractured sandstone. However, their models primarily focus on reactive fluid flow within fractured porous media rather than on the fracturing behavior influenced by the reactive fluid. In summary, most existing computational frameworks for the coupled chemical-hydro-mechanical process of fracturing in porous media, use simplified reaction models and rarely couple acid flow with hydraulic fracture to investigate the effects of the detailed chemical reactions on fracture initiation and propagation.

This paper presents a comprehensive framework for addressing the coupled chemohydro-mechanical problems encountered in sandstone acidizing and hydraulic fracturing processes. The proposed framework encompasses various phenomena, including fluid flow in poroelastic media, diffusion-advection transport of acid components, their reactions with the solid matrix, pore pressure diffusion, solid deformation, dissolution/precipitation of multi-mineral systems, mechanical failure, and chemo-assisted fracturing. This framework utilizes the phase-field approach, in which fractures are treated as narrow diffusive transitional entities with the same dimension as the solid matrix in mechanical problems. Consequently, the multi-physical fields associated with acid fluid transport are solved within the computational domain at the continuum scale.

Specifically, we derive the mass balance and momentum balance governing equations, taking into account elastic potential energy, fracture fluid energy, pore fluid energy, crack dissipation energy, and external source energy contributions to the total potential energy functional. Additionally, we derive the corresponding conjunction fracture mechanics by combining expressions for crack driving force that considers elastic potential energy, pore fluid pressure, and the forces acting on the crack sides.

When considering the elastic potential energy, we introduce a degradation function to indicate the state of the porous media, distinguishing between the broken and unbroken regions. In the proposed framework, we account for both mechanical and chemical degradation. Building upon previous research (Schuler et al., 2020), we define chemical degradation to align with mechanical damage, represented by an exponential function of porosity changes. However, the empirical relations proposed by Bringedal et al. (2020) and Schuler et al. (2020) do not explicitly account for changes in porosity. Instead, the dissolution/precipitation of multi-minerals is represented using implicit mass balance equations of chemical components and the volumetric fraction of minerals, which illustrates the resulting porosity changes. Regarding the fracture fluid energy, we approximate the pressure force acting on the fracture sides with the fluid energy represented by the gradient of the phase field. This approximation preserves the  $\Gamma$ -convergence property, as demonstrated in previous work (Chukwudozie et al., 2019). For the pore fluid energy, we utilize the phase field as an indicator and combine it with the elastic potential energy to derive an extended form of the poroelastic equations for the porous media. This approach specifically considers the effects of pore pressure and elasticity outside of the crack. The degradation of materials is updated by both fracture mechanics and chemical degradation. As a result, we reformulate the historical driving force of the phase field to account for these combined degradation mechanisms.

We emphasize that the conservation laws formulated for chemically-reacting porous media in this paper are specifically tailored to the sandstone acidizing process. However, the framework for the coupled chemo-mechanical response integrated with the phase-field modeling approach is applicable in a general context. The transport of multiple acid components involves diffusion, advection, and source/sink mechanisms. The model incorporates source and sink terms to account for external activities such as injection and production, as well as internal dynamics like kinetic reactions and intra-aqueous exchanges among various chemical species. This study builds on the previous work conducted by Guo and Na (2023) to extend the inclusion of kinetic and intra-aqueous reactions as source/sink terms within the transport equation.

The corresponding dissolution/precipitation of multi-minerals is then captured through mass balance equations, allowing for the characterization of fast- and slow-reacting phenomena in sandstone acidizing engineering. The changes in porosity and permeability are phenomenologically characterized by the mass exchange of fast- and slow-reacting minerals. To validate the accuracy of our framework, we present three numerical examples. First, we examine the classical single-slit crack problem proposed by Miehe et al. (2010a) to assess our framework's capability to predict crack propagation in a solid domain. Second, we analyze the impact of porosity alterations on the chemo-mechanical degradation of porous media. We then verify the performance of our framework in conventional fluid-driven problems encountered in hydraulic fracturing scenarios. Analytical solutions are employed to validate the reliability and accuracy of our model. Furthermore, we conduct a benchmark for the multi-mineral reaction systems to demonstrate the capability of our framework in predicting coupled chemo-hydro-mechanical fracturing problems. This benchmark serves to showcase the distinctions between mechanical fracture and chemo-mechanical fracture properties, providing valuable insights into their respective behaviors.

The remaining content is structured as follows: Section 3.2 introduces the theoretical framework of the phase-field modeling approach for chemo-assisted cracking in poroelastic media. This includes descriptions of the proposed phase-field method, poromechanics, and the total potential energy. Section 3.3 presents the balance principles governing the solid and fluid constituents of the system, exploring the conservation laws associated with them. In Section 3.4, we delve into the constitutive response of the system, examining the mass exchange resulting from chemical reactions and the hydromechanical response arising from alterations in material properties. Section 3.5 focuses on establishing a coupling scheme that effectively integrates the various components of the model. Numerical examples are provided in Section 3.6 to demonstrate the application and effectiveness of the proposed model. Finally, Section 3.7 concludes the manuscript, highlighting the capabilities of the model and presenting future research directions.

# 3.2 Phase-field modeling approach for the chemo-assisted crack in poroelastic media

In this section, we introduce the phase field modeling approach to address the multiphysics problems associated with crack propagation in porous media induced by reactive flow. We begin by presenting the classical smooth approximation of crack topology and illustrating the phase field variable as a damage parameter to distinguish between the reservoir and the crack. The regularization length scale parameter, which controls the size of the diffusive zone between the reservoir and the crack, is then discussed, Next, we describe the displacement of the solid in non-fractured porous media and the system for fluid diffusion, utilizing the phase field parameters as indicator variables to differentiate between different flow types. Based on these concepts, we establish a variational approach based on the potential energy of the system, encompassing five components: the effective strain energy stored in the solid skeleton, the dissipation of energy due to cracking, the energy stored in the crack fluid, the energy stored in the pore fluid, and the external energy source.



FIGURE 3.1: Schematics of a problem domain with boundary conditions. Here we denote the intact porous media domain as  $\Omega$  and fractures as surface  $\Gamma$ . (a) A force working body with cracks; (b) A transverse interface with cracks; (c) A transverse interface with cracks approximated by a diffusion zone.

First, we define a domain comprising a porous reservoir that contains a fixed crack with a transition zone, as shown in Figure 3.1. Let  $\Omega \in \mathbb{R}^d$ , d = 1, 2, 3, represent a smooth, open, and bounded computational domain. The computational domain  $\Omega$  contains a crack, considered as a thin three-dimensional body (or a two-dimensional area) that is significantly larger than the pore size of the porous medium. We denote the volumes of the reservoir and the crack as  $\Omega_R$  and  $\Omega_F$ , respectively. It is evident that  $\Omega = \Omega_R \cup \Omega_F$ . Regarding the boundaries of the subdomains  $\Omega_F$  and  $\Omega_R$ , the crack surface is denoted as  $\Gamma_F := \Omega_R \cap \Omega_F$ , while the boundary of the reservoir is  $\partial \Omega_R := \partial \Omega_D \cup \partial \Omega_N$ , where  $\partial \Omega_D$ and  $\partial \Omega_N$  represent the Dirichlet and Neumann boundary conditions, respectively.

### 3.3 Phase field approximation of crack topology

In this study, we employ the phase-field approach (Miehe et al., 2010a; Bourdin et al., 2008) to represent the fracture volume  $\Omega_F$ , as depicted in Figures 3.1(b) and (c). The sharp crack surface  $\Gamma$  is replaced by the regularized crack surface  $\Gamma_F$ . For instance, in

the case of a cracked bar in 1D located at the axial position x = 0,  $\Gamma$  represents the fully broken surface. The regularized crack topology is described by a man-made smeared field variable  $\phi \in [0, 1]$ , referred to as the crack phase field. Specifically,  $\phi = 0$  characterizes the unbroken state, while  $\phi = 1$  corresponds to the fully broken state of the material. The transition state can be approximated by the exponential function  $\phi(x) = e^{-|x|/l_0}$ . Figure 3.2 illustrates the aforementioned concept, and more details can be found in the work of Miehe et al. (2010b). In line with the approach proposed by Miehe et al.



FIGURE 3.2: Crack discontinuity at x = 0 and diffusive crack at x = 0 modelled with a length scale  $l_0$  (Miehe et al., 2010b).

(2010b), we approximate the total fracture surface area  $A_{\Gamma_F}$  using a fracture surface density functional  $\gamma_{l_0}$  that depends on the crack phase-field  $\phi$  and its gradient, as follows,

$$A_{\Gamma_F} \approx A_{\Gamma_{l_0}} = \int_{\Omega} \gamma_{l_0}(\phi, \nabla \phi) d\Omega, \qquad (3.1)$$

where,

$$\gamma_{l_0}(\phi, \nabla \phi) = \frac{\phi^2}{2l_0} + \frac{l_0}{2} (\nabla \phi \cdot \nabla \phi).$$
(3.2)

The theoretical foundation of the classical brittle fracture in solids was established by Griffith (1921); Irwin et al. (1967), and Barenblatt (1962). The Griffith-type theory provides a criterion for crack propagation but is insufficient for determining the curvilinear crack paths, crack kinking, and crack branching, especially in predicting crack initiation. Francfort and Marigo (1998) suggested using variational methods based on energy minimization to overcome these challenges. Bourdin et al. (2000, 2008) incorporated a regularization setting in their framework, obtaining results through  $\Gamma$ -convergence, inspired by image segmentation technology. Various local dissipation functions have been proposed to model brittle fracture in the regularization of the variational theory of brittle fracture. Several dissipation functions control the shape of the regularized profile of the phase field (Clayton and Knap, 2011; Mesgarnejad et al., 2015; Bleyer and Alessi, 2018). In this study, we adopt the standard quadratic local dissipation model (Dittmann et al., 2020). Therefore, the fracture energy can be integrated over the entire domain, can be expressed as follows:

$$\Psi_c = \int_{\Omega} g_c \gamma_{l_0}(\phi, \nabla\phi) d\Omega = \int_{\Omega} \frac{g_c}{l_0} \left[\frac{\phi^2}{2} + \frac{l_0^2}{2} (\nabla\phi \cdot \nabla\phi)\right] d\Omega,$$
(3.3)

where  $g_c$  symbolizes the critical Griffith-type energy release rate, defining the energy dissipation within the crack for each unit of the newly formed fracture surface area. For the degradation function  $g(\phi)$ , we adopt the commonly used quadratic function (Bourdin et al., 2000). This quadratic function represents the relationship between the responses of the completely broken and unbroken porous media.

$$g(\phi) = (1 - \phi)^2 + k,$$
 (3.4)

where the parameter k is chosen to be a small value  $(0 < k \ll 1)$  to prevent the tensile part of elastic energy density from vanishing and causing the numerical singularity as the phase-field variable  $\phi$  approaches 1. Throughout this study, we adopt a value of  $k = 10^{-9}$ .

### **3.4** Poroelasticity of porous medium

We first assume that the porous media functions as linear elastic media, experiencing infinitesimal deformations. The displacement of the solid matrix and the diffusive flow within the porous media are governed by the classical quasi-static elliptic-parabolic system  $(\boldsymbol{u}/p)$ , which applies to linear elastic, isotropic, and homogeneous saturated porous solids. In our system, we assume that both the solid grains and the pore fluid are incompressible.

In this case, the total Cauchy stress tensor  $\sigma$  can be decomposed as the sum of the effective stress tensor  $\sigma'$ , which depends solely on the deformation of the solid skeleton, and the interstitial fluid pressure p, as follows,

$$\boldsymbol{\sigma}(\boldsymbol{u}, p) = \boldsymbol{\sigma}'(\boldsymbol{u}) - p\boldsymbol{I}, \qquad (3.5)$$

where  $\boldsymbol{u} \in \mathcal{R}^d$  (d = 1, 2, 3) denotes the displacement of the solid skeleton, p represents the fluid pressure, and  $\boldsymbol{I}$  denotes the identity tensor.

Furthermore, we express the effective stress of the solid skeleton using a linear elastic relationship, as follows,

$$\sigma'(u) = \mathbb{C}^e : \epsilon = (\lambda \mathbf{1} \otimes \mathbf{1} + 2G\mathbf{I}) : \epsilon$$
(3.6)
where  $\lambda = \frac{3Kv}{1+v}$  represents the first Lamé constant;  $G = \frac{3K(1-2v)}{2(1+v)}$  is the second Lamé constant. In our model, we specify the values for the bulk modulus K of the solid skeleton and Poisson's ratio v. The Lamé coefficients can be calculated using the relationships between these elastic constants.  $\mathbb{C}^e$  denotes the fourth-order elastic modulus tensor. **1** is the second-rank identity tensor, with components  $\delta_{ij}$  representing the Kronecker delta. Under the small-strain assumption,  $\epsilon$  serves as the strain measure and is defined as  $\epsilon = \frac{\nabla u + \nabla u^T}{2}$ .

#### 3.4.1 Fluid pressure in fracture and porous matrix

As depicted in the computational domain sketch shown in Figure 3.1, the division of the domain introduces variations in the flow problem, due to the sharp changes in material properties. We assume that the flow, whether in the reservoir's porous media or the fracture, obeys Darcy's law. Specifically, the phase-field variable serves as an indicator to distinguish the different flow pressure equations in each subdomain. Initially, we separate the flow pressure system, treating the fluid in the reservoir and the fluid in the fracture as distinct entities. We adopt the uniform mass continuity equations as presented by Lee et al. (2017),

$$\partial_t (\rho_F \psi_F^{\star}) + \nabla \cdot (\rho_F \tilde{\boldsymbol{v}}_F) = q_F - q_L; \partial_t (\rho_R \psi_R^{\star}) + \nabla \cdot (\rho_R \tilde{\boldsymbol{v}}_R) = q_R,$$
(3.7)

where  $\rho_F$  and  $\rho_R$  represent the fluid densities in fractured and intact porous media, respectively. while  $q_F$  and  $q_R$  denote the source or sink terms for fracture and reservoir, respectively. Additionally,  $q_L$  represents the leak-off term, which is assumed to be 0 in this study.  $\psi_F^*$  and  $\psi_R^*$  are fracture and reservoir fluid, respectively. In our system, we model the problem as involving a saturated, quasi-static material with both the solid and fluid constituent phases being incompressible. In this case,  $\psi_R^* := \nabla \cdot \boldsymbol{u}$ , where  $\boldsymbol{u}$  is the solid displacement. Simultaneously, we set  $\psi_F^* := 1$  reflecting the assumption that the porosity of the fracture is 1. Then, we can express Darcy's law, which governs fluid behavior within the porous media and fractures, in the following general form:

$$\tilde{\boldsymbol{v}}_i = -\frac{\boldsymbol{K}_i}{\nu_i} \cdot (\nabla p_i + \rho_i \boldsymbol{g}); \ i = \{F, R\},$$
(3.8)

where  $K_i$  is the permeability,  $\nu_i$  is the fluid viscosity, and g is gravity.

Consequently, the above uniform mass continuity equations can be rewritten as follows,

$$\frac{\partial(\rho_R \nabla \cdot \boldsymbol{u})}{\partial t} + \nabla \cdot (\rho_R \tilde{\boldsymbol{v}}_R) - q_R = 0,$$
  

$$\nabla \cdot (\rho_F \tilde{\boldsymbol{v}}_F) - q_F = 0.$$
(3.9)

To formulate a unified formulation of the mass balance equations as presented in Eq. (3.9) and to effectively handle the transition of material properties between intact and damaged porous media, we adopt an approach proposed by Lee et al. (2017). To achieve this, we introduce indicators into the combined equation, utilizing the phase-field parameter in the following relationships shown in Figure 3.3:

$$\chi_R(\cdot,\phi) = 1 \text{ in } \Omega_R(t), \text{ and } \chi_R(\cdot,\phi) = 0 \text{ in } \Omega_F(t); \tag{3.10}$$

$$\chi_F(\cdot,\phi) = 1 \text{ in } \Omega_F(t), \text{ and } \chi_F(\cdot,\phi) = 0 \text{ in } \Omega_R(t), \tag{3.11}$$

Thus,  $\chi_R(\cdot, \phi)$  is zero in the fracture domain, and  $\chi_F(\cdot, \phi)$  is zero in the reservoir domain. The diffusion zone is defined using the linear functions below, with  $c_1$  and  $c_2$  as threshold values to differentiate between the fracture and reservoir.

$$\chi_F(\cdot,\phi) = \frac{c_2 - \phi}{c_2 - c_1},\tag{3.12}$$

$$\chi_R(\cdot, \phi) = \frac{\phi - c_1}{c_2 - c_1},\tag{3.13}$$

We can now introduce these indicators into uniform mass continuity equations, simplifying



FIGURE 3.3: The sketch of fracture, intact porous media, and diffusion zone; and the linear indicator functions  $\chi_F$  and  $\chi_R$  linearized by the adjustable parameters  $c_1$  and  $c_2$ . (a) The phase field example for different zones; (b) the sketch of the geometric definition of different zones; (c) linear interpolations of different zones.

them into a compact formula as follows:

$$\frac{\partial(\rho\chi_R\nabla\cdot\boldsymbol{u})}{\partial t} + \nabla\cdot(-\rho\frac{\boldsymbol{K}}{\nu}\cdot(\nabla p + \rho\boldsymbol{g})) - q = 0, \qquad (3.14)$$

where the coefficients of Eq. (3.14) are interpolated using the indicators between the reservoir and fracture, which are listed as below:

$$\rho = \chi_R \rho_R + \chi_F \rho_F, \tag{3.15}$$

$$\nu = \chi_R \nu_R + \chi_F \nu_F, \tag{3.16}$$

$$q = \chi_R q_R + \chi_F q_F \tag{3.17}$$

$$\boldsymbol{K} = \chi_R \boldsymbol{K_R} + \chi_F \boldsymbol{K_F}. \tag{3.18}$$

## 3.4.2 Total potential energy of the system and effective stress principle

The total potential energy governs the principle of effective stress and the evolution of cracks in the system. In this section, we decompose the total potential functional into multiple components to delve deeper into the physical significance of each component. Francfort and Marigo (1998) and Bourdin et al. (2008) introduced a phase-field approximation of the variational formulation for Griffth's theory of brittle fracture. This approach is based on the work of Mumford and Shah (1989) that involves the minimization of the total potential energy of the entire system. In this framework, the total elastic energy released in the computational domain is balanced by the newly developed surface energy associated with fracture propagation. Consequently, studying the potential energy of the entire system is essential for deriving the governing equations for crack propagation. The first variation of the potential energy functional yields the principles of crack propagation, occurring when the system's potential energy attains its minimum value. In this study, the potential energy comprises several components, including the dissipation of energy due to cracking  $\Psi_d$ , the elasticity potential energy in the bulk of solid  $\Psi_e$ , the energy stored in the fracture fluid  $\Psi_f$ , the energy stored in the porous fluid  $\Psi_p$ , and the external source of energy  $\Psi_s$ . We note that the chemical surface energy is ignored in the global coupling formulations; instead, it is considered in the constitutive model as a material property to trigger cracks in Chapter 4. These components are expressed as follows,

$$\Psi = \Psi_d + \Psi_e + \Psi_f + \Psi_p - \Psi_s. \tag{3.19}$$

The elasticity potential energy in the intact porous media is given by,

$$\Psi_e = \int_{\Omega} \psi_e(\boldsymbol{\epsilon}) d\Omega, \qquad (3.20)$$

and the energy density function  $\psi_e$  can be further expressed as,

$$\psi_e(\boldsymbol{\epsilon}) = \frac{1}{2} (\boldsymbol{\sigma'} \cdot \boldsymbol{\epsilon}) = \frac{\lambda}{2} \operatorname{tr}(\boldsymbol{\epsilon})^2 + \nu \operatorname{tr}(\boldsymbol{\epsilon^2}), \qquad (3.21)$$

To couple the phase field and mechanical field, we adopt the concept of damage mechanics, establishing a direct correlation between the evolution of the phase field and crack propagation. This concept is achieved by embedding a degradation function  $g(\phi)$ into the energy function, which represents the solid materials' stiffness reduction as cracks develop. Miehe et al. (2010a,b) exploited the phase filed theories for brittle fracture and gradient-enhanced damage models. They introduced the damage format in phase-field models for brittle fracture, incorporating the degradation function and a damage loading function to ensure the irreversibility of damage. As discussed in Section 3.3, the quadratic polynomial is commonly used as the degradation function. This preference is driven by the mathematical demonstration of  $\Gamma$ - convergence for the phase field with this degradation function. The quadratic degradation function satisfies certain properties to achieve the degradation purpose

$$\begin{cases} g(\phi) \in [0,1], \phi \in [0,1], \\ g'(\phi) \le 0, \phi \in [0,1], \\ g'(1) = 0. \end{cases}$$
(3.22)

To address this issue, we follow the approach suggested by Miehe et al. (2010a) and adopt a spectral decomposition of the tension-compression formulation. This treatment allows for consideration of degradation only in tension. As a result, the elasticity potential energy can be decomposed into tension and compression parts, with the degradation effects applied specifically to the tension part. This can be expressed as follows,

$$\Psi_e(\boldsymbol{\epsilon}, \phi) = \int_{\Omega} g(\phi) \psi_e^+(\boldsymbol{\epsilon}) + \psi_e^-(\boldsymbol{\epsilon}) d\Omega, \qquad (3.23)$$

where  $\psi_e^+(\boldsymbol{\epsilon})$  and  $\psi_e^-(\boldsymbol{\epsilon})$  represent the potential energy generated by the tensile and compressive components, respectively. These two split compositions of strain tensors can

be achieved by considering the positive and negative components of the strain, given by,

$$\Psi_e^{\pm}(\boldsymbol{\epsilon}) = \frac{\lambda}{2} tr(\boldsymbol{\epsilon})^{\pm 2} + \nu tr(\boldsymbol{\epsilon}^{\pm 2}), \qquad (3.24)$$

where the strain tensor  $\boldsymbol{\epsilon}$  is decomposed as follows,

$$\begin{cases} \boldsymbol{\epsilon}^{+} = \sum_{\delta=1}^{d} \epsilon_{\delta}^{+} \boldsymbol{n}_{\delta} \otimes \boldsymbol{n}_{\delta}, \\ \boldsymbol{\epsilon}^{-} = \sum_{\delta=1}^{d} \epsilon_{\delta}^{-} \boldsymbol{n}_{\delta} \otimes \boldsymbol{n}_{\delta}. \end{cases}$$
(3.25)

where  $\epsilon_{\delta}$  denotes the principal strain values, and we define  $\epsilon_{\delta}^{\pm} := (\epsilon_{\delta} \pm |\epsilon_{\delta}|)/2$ . The tensor  $n_{\delta}$  represents the principal strain directions corresponding to the principal strain  $\epsilon$ . The calculation of the eigenvalues is performed using the following procedure (Borja, 2013),

$$\boldsymbol{n}_{\boldsymbol{\delta}} \otimes \boldsymbol{n}_{\boldsymbol{\delta}} = \frac{1}{\prod_{i \neq j}^{\delta} (\epsilon_i - \epsilon_j)} \prod_{i \neq j}^{\delta} (\boldsymbol{\epsilon}_{ij} - \epsilon_i \boldsymbol{I}).$$
(3.26)

In addition, the relationship between strain and stress is essential for calculating the total stress of the system in Eq. (3.5). The effective stress can be derived from the decomposed elastic energy as expressed in Eq. (3.24) as follows,

$$\boldsymbol{\sigma}' = \frac{\partial \Psi_e}{\partial \boldsymbol{\epsilon}} = g(\phi) \frac{\partial \Psi_e^+}{\partial \boldsymbol{\epsilon}} + \frac{\partial \Psi_e^-}{\partial \boldsymbol{\epsilon}}$$
(3.27)

Regarding the potential energy stored in the porous fluid, we adopt a definition proposed by Santillán et al. (2018) introducing a localized potential energy density function to capture the energy stored in the intact porous media. This definition establishes a connection between the degradation function and the fluid energy density, thus eliminating the need for time considerations related to cracking. The redefined potential energy stored in the porous fluid is given as follows,

$$\Psi_p = \int_{\Omega} g(\phi) \psi_p(p, \nabla \cdot \boldsymbol{u}) d\Omega = -\int_{\Omega} g(\phi) p \nabla \cdot \boldsymbol{u} d\Omega.$$
(3.28)

Next, we will express the energy  $\Psi_f$  stored in the fluid within the fracture. To approximate the work done by the pressure force acting along the cracks, we adopt the approach proposed by Chukwudozie et al. (2019). This approximation has proven to be reasonable, and we utilize it as follows,

$$\Psi_f = -\int_{\Gamma} p \parallel \boldsymbol{u} \parallel \boldsymbol{n_{\Gamma}} d\Gamma \cong -\int_{\Omega} p \boldsymbol{u} \cdot \nabla \phi d\Omega.$$
(3.29)

The external source of energy  $\Psi_s$  is given by,

$$\Psi_s = \int_{\Omega} \boldsymbol{f} \cdot \boldsymbol{u} d\Omega + \int_{\partial \Omega_N} \boldsymbol{t} \cdot \boldsymbol{u} dS$$
(3.30)

where f is the body force, and t is the vector of the externally applied forces. Finally, the total potential energy is the combination of the above five components, which can be written as follows:

$$\Psi = \int_{\Omega} G_c \left( \frac{1}{2l_0} \phi^2 + \frac{l_0}{2} |\nabla \phi|^2 \right) d\Omega + \int_{\Omega} \left[ g(\phi) \psi_e^+ + \psi_e^- \right] d\Omega - \int_{\Omega} p \boldsymbol{u} \cdot \nabla \phi d\Omega - \int_{\Omega} g(\phi) p \nabla \cdot \boldsymbol{u} d\Omega + \int_{\Omega} \boldsymbol{f} \cdot \boldsymbol{u} d\Omega + \int_{\partial \Omega_N} \boldsymbol{t} \cdot \boldsymbol{u} dS. \quad (3.31)$$

## 3.5 Conservation laws for chemical-reacting porous media

In this section, we derive the balance principles for the system governing brittle fracture in saturated porous media, taking into account the chemical reactions between the fluid and minerals. As discussed in Section 3.1, sandstone acidizing entails chemical reactions involving multiple minerals, including both fast and slow reactions. Guo and Na (2023) investigated the effects of poro-geochemistry on poromechanics, concluding that changes in geomaterial properties, such as permeability and porosity, have a direct impact on the mechanical response. To capture mass exchange between the acid fluid and solid rock, as well as the mass of minerals, we establish a multi-stage reactive transport model and introduce multi-component reactions as source terms in the mass balance equation. We also introduce volume fraction equations for the fast-reacting and slow-reacting minerals to quantify the dissolution/precipitation mass of the solid. We use these volume fractions to update the porosity alteration, employing constitutive relations described in Section 3.6.1. Additionally, as discussed in Section 3.4.2, we introduce a more direct approximation of the pressure force acting along the sides of the cracks into the total potential energy functional, as shown in Eq. (3.31). This approach enables us to reformulate the linear momentum balance equation. Simultaneously, we derive the corresponding historical strain energy.

#### **3.5.1** Balance of mineral mass

In the field of energy recovery engineering, sandstone acidizing plays a crucial role. One commonly used model to describe the chemical reactions involved in this process is Bryant's model, also known as the four-parameter model (Bryant, 1991). This model accounts for primary, secondary, and tertiary reactions during the acidizing process. Recently, Leong et al. (2019) rearranged and refined This geochemical model provides a modified version. In this modified model, the chemical reactions are grouped, and include the following reactions:

$$\delta_1 \mathrm{HF} + \mathrm{M}_1 \to \delta_5 \mathrm{H}_2 \mathrm{SiF}_6 + \mathrm{AlF}_m \tag{3.32}$$

$$\delta_2 \mathrm{HF} + \mathrm{M}_2 \to \delta_6 \mathrm{H}_2 \mathrm{SiF}_6 + \mathrm{AlF}_\mathrm{m} \tag{3.33}$$

$$\delta_4 H_2 SiF_6 + M_1 \to \delta_8 M_3 + AlF_m \tag{3.34}$$

$$\delta_3 \mathrm{HF} + \mathrm{M}_3 \to \delta_7 \mathrm{H}_2 \mathrm{SiF}_6 + \mathrm{H}_2 \mathrm{O} \tag{3.35}$$

where  $\delta_i$  (i = 1, 2, 3, ..., 7, 8) denotes the stoichiometric coefficients, as described by Da Motta et al. (1993). M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub> denote the groups of fast-reacting minerals, slow-reacting minerals, and silica gel Si(OH)<sub>4</sub>, respectively. AlF<sub>m</sub> denotes the fluorides of aluminum.

The mass exchange between the reactive fluid and reacting minerals is influenced by mineral reactions, as shown in Eqs.  $(3.32)\sim(3.35)$ . Indeed, the kinetic reactions of mineral dissolution/precipitation are governed by the actual reaction rate, which varies depending on the reaction conditions. The interaction between the fluid and the minerals plays a crucial role in determining the rate at which the reaction occurs. The acid consumption, the specific surface area of the minerals, and the reaction rate constant determines the intensity of mass exchange.

First, we define the concentration of acid species  $c_i$ ,  $(i = \text{HF}, \text{H}_2\text{SiF}_6)$ , which are detailed in Section 3.5.2. The aforementioned characterization of the actual reaction rate can be expressed as follows,

$$R_i = E_i \cdot c_i \cdot S_i^\star, \tag{3.36}$$

where  $E_i$  is the reaction rate constant,  $S_j^{\star}$  is the specific surface area of the  $j^{th}$  mineral, and  $R_i$  corresponds to the actual reaction rate. The reaction rate constant is determined by factors such as the reaction activation energy and temperature. This relationship can be described by the Arrhenius equation (Gdanski, 1999, 2000; Economides et al., 2013) given as follows,

$$E_i = E_{i0} exp[\frac{E_{a,i}(T - T_0)}{RTT_0}],$$
(3.37)

where  $E_{i0}$  represents the reference reaction constant measured at the reference temperature  $T_0$ ,  $E_{a,i}$  is the corresponding reaction activation energy, and R is the ideal gas constant. T is temperature, measured in Kelvin scale.

We now present the mass balances for minerals M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub>, respectively,

$$\partial_t ((1-n)c_{\mathrm{M}_1}) + \frac{M_{\mathrm{HF}}S_1^{\star}c_{\mathrm{M}_1}(1-n)\beta_1 E_1 c_{\mathrm{HF}}}{\rho_{\mathrm{M}_1}} + \frac{M_{\mathrm{H}_2\mathrm{SiF}_6}S_1^{\star}c_{\mathrm{M}_1}(1-n)\beta_4 E_4 c_{\mathrm{H}_2\mathrm{SiF}_6}}{\rho_{\mathrm{M}_1}} = 0,$$
(3.38)

$$\partial_t ((1-n)c_{\rm M_2}) + \frac{M_{\rm HF}S_2^{\star}c_{\rm M_2}(1-n)\beta_2 E_2 c_{\rm HF}}{\rho_{\rm M_2}} = 0, \qquad (3.39)$$

$$\partial_t (nc_{\mathrm{M}_3}) + \frac{M_{\mathrm{HF}} S_3^{\star} c_{\mathrm{M}_3} n \beta_3 E_3 c_{\mathrm{HF}}}{\rho_{\mathrm{M}_3}} - \frac{M_{\mathrm{H}_2 \mathrm{SiF}_6} S_1^{\star} c_{\mathrm{M}_1} (1-n) \beta_4 E_4 c_{\mathrm{H}_2 \mathrm{SiF}_6}}{\rho_{\mathrm{M}_1}} \frac{\delta_8 M_{\mathrm{M}_3}}{M_{\mathrm{M}_1}} = 0, \ (3.40)$$

where  $M_{\rm HF}$  and  $M_{\rm H_2SiF_6}$  are the molecular masses of the acid chemical species HF and  $\rm H_2SiF_6$ , respectively.  $M_{\rm M_1}$ ,  $M_{\rm M_2}$ , and  $M_{\rm M_3}$  are the relative molecular masses of the corresponding minerals.  $\beta_1 \sim \beta_4$  denote the dissolution coefficients of HF reacting with fast-reacting minerals  $\rm M_1$ , HF reacting with slow-reacting minerals  $\rm M_2$ , HF reacting with precipitation minerals (silica gels  $\rm M_3$ ), and  $\rm H_2SiF_6$  reacting with fast-reacting minerals  $\rm M_1$ , respectively. The properties  $\rho_{\rm M_1}$ ,  $\rho_{\rm M_2}$ , and  $\rho_{\rm M_3}$  are the densities of the corresponding minerals, with n being the porosity of the porous media.

#### 3.5.2 Balance of chemical species

The acid chemical species HF and  $H_2SiF_6$  are transported through both the reservoir and the fracture. To describe the distribution of acid concentration, we need to consider the transport equations for acid flow in both the reservoir and the fracture. These equations are analogous to the fluid pressure equations discussed in Section 3.4.1. Considering the crack aperture defined in Eq. (3.57), the balance equations for the chemical species can be expressed as follows:

$$\partial_t (H_1 n + H_2 w) c_{\rm HF} + \nabla \cdot ((H_1 n + H_2 w) \boldsymbol{v} \cdot c_{\rm HF}) - \nabla \cdot ((H_1 n + H_2 w) \boldsymbol{D}_{\rm HF} \cdot \nabla c_{\rm HF}) + \sum_{\rm mineral=1}^3 (E_i c_{\rm M_i} (H_1 \cdot S_i^{\star} (1-n) + H_2)) = 0,$$
(3.41)

$$\partial_{t}(H_{1}n + H_{2}w)c_{H_{2}SiF_{6}} + \nabla \cdot ((H_{1}n + H_{2}w)\boldsymbol{v} \cdot c_{H_{2}SiF_{6}}) - \nabla \cdot ((H_{1}n + H_{2}w)\boldsymbol{D}_{H_{2}SiF_{6}} \cdot \nabla c_{H_{2}SiF_{6}}) + (H_{1} \cdot S_{1}^{\star}(1-n) + H_{2})E_{4}c_{M_{1}}c_{H_{2}SiF_{6}} - \sum_{\text{mineral}=1}^{3} \frac{\delta_{i+4}}{\delta_{i}}(E_{i}c_{M_{i}}c_{HF}(H_{1} \cdot S_{i}^{\star}(1-n) + H_{2})) = 0,$$

$$(3.42)$$

where  $D_{\text{HF}}$  and  $D_{\text{H}_2\text{SiF}_6}$  are the diffusion tensors of the chemical species HF and  $\text{H}_2\text{SiF}_6$ , respectively, and w represents the crack aperture, with a detailed definition provided in Section 3.6.2. The functions  $H_1$  and  $H_2$  are Heaviside step functions used to differentiate between various flow types in the reservoir and fracture, respectively.

$$H_1(\phi - 0.5) := \begin{cases} 0, \text{ if } \phi - 0.5 \le 0, \\ 1, \text{ if } \phi - 0.5 > 0, \end{cases}; \ H_2(\phi - 0.5) := \begin{cases} 1, \text{ if } \phi - 0.5 \le 0, \\ 0, \text{ if } \phi - 0.5 > 0. \end{cases}$$
(3.43)

### 3.5.3 Balance of linear momentum and crack evolution

The initiation, propagation, and branching of cracks can be determined through the minimization of the potential energy, using the variational approach (Francfort and Marigo, 1998). Accordingly, the variational formulation of the total potential energy and the corresponding boundary conditions can be expressed as follows:

$$\begin{cases} \delta \Psi = \int_{\Omega} (\frac{\partial \Psi}{\partial \boldsymbol{u}} - \nabla \cdot \frac{\partial \Psi}{\partial \nabla \boldsymbol{u}}) \delta \boldsymbol{u} d\Omega + \int_{\Omega} (\frac{\partial \Psi}{\partial \phi} - \nabla \cdot \frac{\partial \Psi}{\partial \nabla \phi}) \delta \phi d\Omega = 0, \text{ in } \Omega, \\ \frac{\partial \Psi}{\partial \nabla \boldsymbol{u}} \cdot \boldsymbol{n} = \boldsymbol{t}; \frac{\partial \Psi}{\partial \nabla \phi} \cdot \boldsymbol{n} = 0, \text{ in } \partial_{N} \Omega. \end{cases}$$
(3.44)

Next, we derive the Fréchet derivative terms with respect to  $\boldsymbol{u}$  and  $\phi$ , enabling the formulation of the minimization problem's strong form.

$$\frac{\partial \Psi}{\partial \boldsymbol{u}} - \nabla \cdot \frac{\partial \Psi}{\partial \nabla \boldsymbol{u}} = \nabla \cdot (\boldsymbol{\sigma}' - g(\phi)p\boldsymbol{I}) + p\nabla\phi + \boldsymbol{f}, in \ \Omega$$
(3.45)

$$\frac{\partial \Psi}{\partial \phi} - \nabla \cdot \frac{\partial \Psi}{\partial \nabla \phi} = \frac{G_c}{l_0} (\phi - l_0^2 \nabla^2 \phi) - 2(1 - \phi)(\psi_e^+(\epsilon) - p\nabla \cdot \boldsymbol{u}) - \nabla \cdot (p\boldsymbol{u}), in \ \Omega.$$
(3.46)

Therefore, the first variation of the function can be given as follows:

$$\delta \Psi = \int_{\Omega} [\nabla \cdot (\boldsymbol{\sigma}' - g(\phi)p\boldsymbol{I}) + p\nabla\phi + \boldsymbol{f}] \delta \boldsymbol{u} d\Omega - \int_{\partial_{N}\Omega} [(\boldsymbol{\sigma}' \cdot \boldsymbol{n} - g(\phi)p\boldsymbol{n}) - \boldsymbol{t}] \delta \boldsymbol{u} dS + \int_{\Omega} [\frac{G_{c}}{l_{0}} (\phi - l_{0}^{2}\nabla^{2}\phi) - 2(1 - \phi)(\psi_{e}^{+}(\boldsymbol{\epsilon}) - p\nabla \cdot \boldsymbol{u}) - \nabla \cdot (p\boldsymbol{u})] \delta \phi d\Omega - \int_{\partial\Omega} [G_{c}l_{0}\nabla\phi \cdot \boldsymbol{n}] \delta \phi dS = 0.$$
(3.47)

To satisfy the arbitrariness of  $\delta u$  and  $\delta \phi$ , we obtain the strong form of the phase-field problem as follows:

$$\begin{cases} \nabla \cdot (\boldsymbol{\sigma}' - g(\phi)p\boldsymbol{I}) + p\nabla\phi + \boldsymbol{f} = \boldsymbol{0}, \\ \frac{G_c}{l_0}(\phi - l_0^2\nabla^2\phi) = 2(1-\phi)(\psi_e^+(\boldsymbol{\epsilon}) - p\nabla\cdot\boldsymbol{u}) + \nabla\cdot(p\boldsymbol{u}), \end{cases}$$
(3.48)

The boundary conditions can be expressed as,

$$\begin{cases} \boldsymbol{u} = \boldsymbol{u}_{\boldsymbol{0}}, \text{ in } \partial\Omega_{D} \\ \boldsymbol{\sigma} \cdot \boldsymbol{n} = \boldsymbol{t}, \text{ in } \partial\Omega_{N} \\ \nabla \boldsymbol{\phi} \cdot \boldsymbol{n} = 0, \text{ in } \partial\Omega. \end{cases}$$
(3.49)

Crack propagation occurs when the strain energy exceeds the critical energy release rate  $G_c$ , thereby allowing the damage or fracture zones to extend. However, in some cases, the strain energy can decrease, indicating the possibility of crack healing. Consequently, the previous strong form of the phase field does not guarantee its irreversibility. To address this concern, we adopt the approach proposed by Miehe et al. (2010b), where a historical variable  $\mathcal{H}$  is introduced to capture the maximum of strain energy over time.

$$\mathcal{H}^{(t+\Delta t)}(\boldsymbol{u}, p, t) := \max\{2(1-\phi)(\psi_e^+(\boldsymbol{\epsilon}) - p\nabla \cdot \boldsymbol{u}) + \nabla \cdot (p\boldsymbol{u})\},$$
(3.50)

To ensure the irreversibility of damage, we always update the value of the historical variable  $\mathcal{H}$  as follows: If  $\mathcal{H}^{(t+\Delta t)}$  is greater than  $\mathcal{H}^t$ , we take the increased value  $\mathcal{H}^{(t+\Delta t)}$ ; otherwise, we keep the historical value  $\mathcal{H}^t$ . By adopting this approach, we can guarantee the irreversibility of the damage process.

## 3.6 Constitutive response

In this section, we focus on the mechanical constitutive response to multi-mineral chemical reactions in the context of sandstone acidizing. We utilize phenomenological relations to capture the effects of mass exchange on the mechanical behaviors of the material. The evolution of mass volume fractions, as described in Section 3.5.1, directly reflects the changes in porosity. Corresponding changes in permeability are expressed using the Kozeny-Carman equation (Carman, 1937). Contrary to previous studies (Schuler et al., 2020; Xie et al., 2023), our multi-stage reactive transport model prioritizes the interaction between the acid fluid and fast-reacting minerals, which more accurately represents the heterogeneous nature of sandstone acidizing. This approach may also induce anisotropic crack propagation. Furthermore, the chemical reactions can result in the degradation of material strength. To account for this degradation, we adopt the chemical degradation function proposed by Schuler et al. (2020) and incorporate experimental data into the elastic constants to reflect material weakening. Finally, we highlight the definition of permeability for both the porous matrix and the fracture. We specifically discuss the characterization of fracture permeability within the phase-field method.

## 3.6.1 Mass exchanges and chemical responses

Mass exchanges between the acid fluid and solid minerals play a crucial role in the chemical response. The local mass conservation principles for fluid and solid, as discussed in Sections 3.4.1 and 3.5.1, govern these exchanges. The chemical responses primarily involve the compositional species of the acid fluid and the volumetric properties of the solid. Compositional species act as source or sink terms, participating in the local chemical equilibrium of acid species such as HF and  $H_2SiF_6$ . These species are incorporated into the transport equations described in Section 3.5.2. The constitutive law for the rate of erosion (dissolution) depends on the underlying physical mechanisms of the erosion process. Some studies, such as Spyropoulos et al. (1999), suggest that the rate of dissolution can be assumed to be proportional to the micro-crack density. A higher micro-crack density exposes a larger surface area to the chemical reaction, thereby influencing the erosion rate. It is worth noting that the accumulation of dissolved minerals can also alter the dynamic viscosity of the fluid (Coussot, 1997). However, these considerations are beyond the scope of this study.

This study utilizes an empirical formula to express the volumetric changes and to characterize the changes in porosity (Kalia and Balakotaiah, 2007). This explicit relation is derived from changes in the volumetric fractions of fast-reacting minerals, slow-reacting minerals, and silica gel. It can be expressed as follows:

$$n = n_0 + (1 - n_0) \sum_{i=1}^{2} (c_{\mathrm{M}_{i0}} - c_{\mathrm{M}_i}) - n_0 (c_{\mathrm{M}_3} - c_{\mathrm{M}_{30}}), \qquad (3.51)$$

where  $c_{M_{i0}}$ , i = 1, 2, 3, represents the initial volumetric fractions of three kinds of minerals.

Alteration of porosity can directly influence the permeability of the porous media. Here, We employ the well-known Kozeny-Carman equation, which is commonly used to model the relationship between porosity and permeability changes caused by mineral dissolution/precipitation (Hommel et al., 2018). The equation expresses the absolute permeability change as follows:

$$\frac{k}{k_0} = \left(\frac{n}{n_0}\right)^3 \left(\frac{1-n_0}{1-n}\right)^2,\tag{3.52}$$

where  $k_0$  and  $n_0$  denote the initial absolute permeability and porosity, respectively.

#### 3.6.2 Hydromechanical responses

The hydromechanical responses consider both damaged and undamaged deformation and hydraulic conductivity. In the case of an undamaged medium, the response of the effective stress principle is influenced by either the weakening or strengthening of the elastic modulus. To capture the influence of porosity, particularly on the elastic modulus, we have adopted reliable data provided by Palchik and Hatzor (2002) and Croizé (2010). The best-fitted curve, as illustrated in Figure 3.4, is employed to represent the relationship between porosity and the corresponding petrophysical property.

In this study, we use the experimental data on elastic properties, which have been verified and employed in numerical simulations by Shovkun and Espinoza (2019). However, it is crucial to note that dealing with extremely large or small porosity values may result in numerical issues when using the fitted curve. To address this issue, we adopt the approach suggested by Shovkun and Espinoza (2019), restricting the minimum and maximum values of the elastic modulus to 1 and 65 GPa, respectively. As a result, the expression for the effective stress in Eq. (3.27) has been suitably modified.

$$\boldsymbol{\sigma}'(\boldsymbol{u}) = (\lambda(E(n))\mathbf{1} \otimes \mathbf{1} + 2G(E(n))\boldsymbol{I}) : \boldsymbol{\epsilon}, \qquad (3.53)$$

where the relations between E and the Lamé coefficients  $\lambda, v$  are  $\lambda = \frac{Ev}{(1+v)(1-2v)}$  and  $G = \frac{E}{2(1+v)}$ .



FIGURE 3.4: Distribution of porosity under chemical reactions with time.

In addition to the mechanical degradation, we also consider the chemical degradation as an additional factor that contributes to the weakening of the damaged area in porous media. Schuler et al. (2020) proposed the chemical damage variable based on the work of Le Bellégo et al. (2003); Pignatelli et al. (2013). The fundamental idea is to relate the chemical damage to changes in rock porosity resulting from mineral dissolution. Several studies have quantified mechanical weakening in terms of parameters, such as bulk modulus and Young's modulus (Bemer et al., 2004; Wojtacki et al., 2015), to propose an exponential relation. As a result, the chemical damage  $\phi^{\text{chem}}$  can be expressed as follows,

$$\phi^{\text{chem}}(n) = e^{-r|\Delta n|},\tag{3.54}$$

where r is a coefficient determined by the experimental data. For this study, we set it to 10. Consequently, we finish the definition of the chemical degradation, and further which results in an expression of the degradation function,

$$g(\phi, \phi^{\text{chem}}) = [(\phi^{\text{chem}})(1-\phi)]^2 + k.$$
(3.55)

Finally, it is necessary to update the degradation effects on porous media in Eqs. (3.23), (3.27), (3.28), (3.29), (3.30), (3.33), and (3.38).

In this study, the fluid flow within the porous media of the reservoir and fracture is assumed to resemble laminar flow of a Newtonian fluid with a significantly lower Reynolds number. It is widely accepted that laminar fluid flow in fractures can be approximated as flow between two parallel plates, increasing permeability along the flow direction. Therefore, fluid flow in the reservoir and fracture is assumed to follow the generalized Darcy's law as described in Eq. (3.14). Considering the porosity and permeability evolution described by Eqs. (3.51) and (3.52), we define the permeability of the reservoir as follows:

$$\boldsymbol{K}_{\boldsymbol{R}} := \begin{cases} \kappa(n) \cdot \begin{bmatrix} \kappa^{xx} & \kappa^{xy} & \kappa^{xz} \\ \kappa^{yx} & \kappa^{yy} & \kappa^{yz} \\ \kappa^{zx} & \kappa^{zy} & \kappa^{zz} \end{bmatrix} & \text{for 3D,} \\ \\ \kappa(n) \cdot \begin{bmatrix} \kappa^{xx} & \kappa^{xy} \\ \kappa^{yx} & \kappa^{yy} \end{bmatrix} & \text{for 2D,} \\ \\ \kappa(n) \cdot \kappa & \text{for 1D,} \end{cases}$$
(3.56)

The permeability of the reservoir is represented by the components  $\kappa^{xx}$ ,  $\kappa^{yy}$ , and  $\kappa^{zz}$ , which corresponds to the permeability in the *x*-, *y*-, and *z*- directions, respectively. The multiplier  $\kappa(n)$  is used to update the permeability tensor  $\mathbf{K}_R$  when the porosity *n* undergoes changes.

The permeability of the fracture is determined by the aperture of cracks using the classical cubic law. The crack aperture is linked to the deformation projected along the normal direction of the cracks. Therefore, the permeability of the fracture can be defined as a function of the crack aperture as follows:

$$\mathbf{K}_{\mathbf{F}} := \frac{1}{12} w^2, \ w = H(\phi - 0.5)[h_e(1 + \mathbf{n}_c \cdot \boldsymbol{\epsilon} \cdot \boldsymbol{n}_c)], \tag{3.57}$$

where w denotes the crack aperture,  $h_e$  is the characteristic length estimated by the minimum finite element size, and  $\epsilon$  is the strain. The unit normal  $n_c$  for the projection is approximated using the gradients of phase field  $\phi$ , calculated as  $n_c = \frac{\nabla \phi}{|\nabla \phi|}$ . The Heaviside step function  $H(\phi)$  is used to identify the initiation of fracture when the solid is half-damaged (Heider and Sun, 2020), where  $H(\phi - 0.5) := 0$ , if  $\phi - 0.5 \leq 0$  and  $H(\phi - 0.5) := 1$ , if  $\phi - 0.5 > 0$ . It is worth mentioning that we ignore the enhanced permeability due to the crack opening for the undamaged porous media. Eq. (3.57) is for the calculation of fracture aperture, that only applies to the completely damaged host matrix As for the precise prediction of the matrix and fracture permeability, it may

require other geometrical features, such as formation factor, tortuosity, or shape pores. (Zhang and Sanderson, 1995; Bogdanov et al., 2007)

## 3.7 Coupling scheme

In this section, we focus on the strategies for solving the coupled problems. We begin with the semi-discrete field equations, detailed in Appendix A.3. First, we introduce the implicit monolithic solving system for mixed finite elements. To enhance computational efficiency, We utilize the block-preconditioned Newton-Krylov solvers for the strongly coupled u/p formulations. We employ a preconditioner specifically designed for the u/psystem (Dawson et al., 1997; White and Borja, 2011). Next, we propose the staggered scheme for solving the remaining formulations. We pay particular attention to the inclusion of stabilization terms to mitigate spurious oscillations near the undrained limit. Additionally, we discuss the split approach for the convection-diffusion-source/sink reactive equation. This approach combines a Taylor-Galerkin discretization technique with a system of ordinary differential equations, solved using a fourth-order Runge-Kutta algorithm. Finally, we present an algorithm to explain the step-by-step solving procedures of the phase-field modelling approach for chemo-assisted cracking in poroelastic media.

## 3.7.1 Combined implicit monolithic and staggered algorithms for chemoassisted cracking

The semi-discrete forms of the governing equations consist of variables  $\boldsymbol{u}$ ,  $\boldsymbol{p}$ ,  $\boldsymbol{\phi}$ ,  $\boldsymbol{c}_{\mathrm{HF}}$ ,  $\boldsymbol{c}_{\mathrm{H_2SiF_6}}$ ,  $\boldsymbol{c}_{\mathrm{M_1}}$ ,  $\boldsymbol{c}_{\mathrm{M_2}}$ , and  $\boldsymbol{c}_{\mathrm{M_3}}$  for the nodal vectors for displacement, pore pressure, phase field, concentration of HF, concentration of H<sub>2</sub>SiF<sub>6</sub>, volume fraction of fast-reacting minerals, volume fraction of slow-reacting minerals, and volume fraction of silica gel, respectively. The discrete forms of the governing field Eqs. (3.36)-1, (3.14), (3.36)-2, (3.48), (3.49), (3.45), (3.46), (3.47) are:

$$\boldsymbol{K}\boldsymbol{u} + \boldsymbol{G}\boldsymbol{p} = \boldsymbol{R}_{\boldsymbol{u}},\tag{3.58}$$

$$H\dot{\boldsymbol{u}} + \boldsymbol{X}\boldsymbol{p} = \boldsymbol{R}_{\boldsymbol{p}},\tag{3.59}$$

$$\boldsymbol{\kappa}\boldsymbol{d} = \boldsymbol{R}_{\boldsymbol{d}},\tag{3.60}$$

$$S_1 \dot{c}_{M_1} + T_1 c_{M_1} = R_{M_1},$$
 (3.61)

$$\boldsymbol{S_2} \dot{\boldsymbol{c}}_{M_2} + \boldsymbol{T_2} \boldsymbol{c}_{M_2} = \boldsymbol{R}_{M_2}, \qquad (3.62)$$

$$\boldsymbol{S_3 \dot{\boldsymbol{c}}}_{\mathrm{M}_3} + \boldsymbol{T_3 \boldsymbol{c}}_{\mathrm{M}_3} = \boldsymbol{R}_{\mathrm{M}_3}, \tag{3.63}$$

$$\boldsymbol{E}_{1} \dot{\boldsymbol{c}}_{\mathrm{HF}} + \boldsymbol{Q}_{1} \boldsymbol{c}_{\mathrm{HF}} = \boldsymbol{R}_{\mathrm{HF}}, \qquad (3.64)$$

$$\boldsymbol{E_2} \dot{\boldsymbol{c}}_{\mathrm{H_2SiF_6}} + \boldsymbol{Q_2} \boldsymbol{c}_{\mathrm{H_2SiF_6}} = \boldsymbol{R}_{\mathrm{H_2SiF_6}}, \qquad (3.65)$$

We note that matrices and vectors in Eqs.  $(3.58) \sim (3.65)$  are not mentioned here, and detailed expressions for the terms in the discrete field equations can be found in Appendix A.3.

A staggered scheme is adopted to update the phase field  $\phi$ ,  $(\boldsymbol{u}, \boldsymbol{p})$ , and set of chemical species and minerals:

$$\{\boldsymbol{c}_{\mathrm{M}_{1}}, \boldsymbol{c}_{\mathrm{M}_{2}}, \boldsymbol{c}_{\mathrm{M}_{3}}, \boldsymbol{c}_{\mathrm{HF}}, \boldsymbol{c}_{\mathrm{H}_{2}\mathrm{SiF}_{6}}.\}$$

Both the *monolithic* and *operator split* schemes are adopted to solve the system of equations. After we decouple the system and give rise to  $\{u, p\}$ ,  $\{\phi, c_{M_1}, c_{M_2}, c_{M_3}, c_{HF}, c_{H_2SiF_6}\}$  parts. Here,  $\{u, p\}$  is a monolithic system, indicating that a single solver is employed to update the field values simultaneously. Since u and p are strongly coupled, the pore pressure and effective stress of the solid highly affect each other. The following field variables  $\phi, c_{M_1}, c_{M_2}, c_{M_3}, c_{HF}, c_{H_2SiF_6}$ , are updated separately. We extend the phase-field approach for cracking to encompass a multiphysical scenario, necessitating a more comprehensive consideration of the strong relationship between the fluid and solid components.

In this case, we present the newly developed combined implicit monolithic and staggered algorithm. We first solve the following block-partitioned system in a monolithic manner,

$$\begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{H} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \dot{\mathbf{u}} \\ \dot{\mathbf{p}} \end{bmatrix} + \begin{bmatrix} \mathbf{K} & \mathbf{G} \\ \mathbf{0} & \mathbf{X} \end{bmatrix} \begin{bmatrix} \mathbf{u} \\ \mathbf{p} \end{bmatrix} = \begin{bmatrix} \mathbf{R}_{\mathbf{u}} \\ \mathbf{R}_{p} \end{bmatrix}, \qquad (3.66)$$

Then, the operator splits for the field variables  $\phi$ ,  $c_{M_1}$ ,  $c_{M_2}$ ,  $c_{M_3}$ ,  $c_{HF}$ ,  $c_{H_2SiF_6}$  are organized

into a matrix but solved separately. The stabilization parameter is essential for the monolithic system presented in Eq. (3.66). It is well known that pore pressure can exhibit spurious oscillation in undrained conditions when the solid displacement and pore pressure are spanned by the same basis function (Brezzi and Bathe, 1990; Murad and Loula, 1994; Zienkiewicz et al., 1999). This issue arises due to the violation of the inf-sup condition (White and Borja, 2008; Sun et al., 2013). To address this problem, either a Ladyzhenskaya-Babuska-Brezzi (LBB)-stable finite element pair or a wide range of stable combinations need to be employed (Pastor et al., 2000; Truty and Zimmermann, 2006; White and Borja, 2008). In this study, we adopt the stabilized formulation proposed by White and Borja (2008), which enables equal-order linear interpolation of the displacement and pressure fields while maintaining optimal convergence. In this case, the matrix system for the problem is shown in Eq. (3.67). We take the time-rate terms and separate them from the remaining terms in a uniform equation, which reads:

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & S_{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & S_{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & E_{1} & 0 \\ 0 & 0 & 0 & 0 & E_{2} \end{bmatrix} \begin{bmatrix} \dot{\phi} \\ \dot{c}_{M_{1}} \\ \dot{c}_{M_{2}} \\ \dot{c}_{M_{3}} \\ \dot{c}_{HF} \\ \dot{c}_{H_{2}SiF_{6}} \end{bmatrix} + \\ \begin{bmatrix} \kappa & 0 & 0 & 0 & 0 & 0 \\ 0 & T_{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & T_{2} & 0 & 0 & 0 \\ 0 & 0 & T_{3} & 0 & 0 \\ 0 & 0 & 0 & T_{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & Q_{1} & 0 \\ 0 & 0 & 0 & 0 & Q_{2} \end{bmatrix} \begin{bmatrix} \phi \\ c_{M_{1}} \\ c_{M_{2}} \\ c_{M_{3}} \\ c_{HF} \\ c_{H_{2}SiF_{6}} \end{bmatrix} = \begin{bmatrix} R_{\phi} \\ R_{c_{M_{1}}} \\ R_{c_{M_{2}}} \\ R_{c_{M_{3}}} \\ R_{c_{HF}} \\ R_{c_{H_{2}SiF_{6}}} \end{bmatrix}, \qquad (3.67)$$

The discrete variational equation for the mass balance also requires an additional timediscrete term, given by:

$$\tau_{STAB} = \int_{\Omega} \frac{1}{2\nu^n \Delta t} (\psi^h - \prod \psi^h) (p_{n+1}^h - \prod p_{n+1}^h - p_n^h + \prod p_n^h) d\Omega$$
(3.68)

where  $\psi^h$  and  $p^h$  are interpolations of the shape function and pressure, respectively.  $\prod \psi^h$ and  $\prod p^h$  are corresponding average values that are defined as:

$$\begin{cases} \prod p^{h} = \frac{1}{V^{e}} \int_{\Omega^{e}} p^{h} d\Omega \\ \prod \psi^{h} = \frac{1}{V^{e}} \int_{\Omega^{e}} \psi^{h} d\Omega \end{cases}$$
(3.69)

where  $V^e$  is the volume of the element and  $\Omega^e$  is the computational domain of the element.

## 3.7.2 Two step stable split for convection-diffusion-source/sink reactive transport problem

The balance equations of chemical species, given by Eqs. (3.41) and (3.42), can pose challenges in terms of convergence and stability in numerical simulations. To address these issues, we employ a two-step splitting technique to solve the concentration transport problem, taking into account the effects of convection, diffusion, and source/sink terms (Fernandez-Merodo et al., 2007). This technique helps to improve the numerical stability and convergence of the solution.

Firstly, the balance equations of chemical species, represented by Eqs. (3.41) and (3.42), is expressed in a general form as:

$$\partial_t \boldsymbol{c_i} + \nabla \cdot (\boldsymbol{v} \cdot \boldsymbol{c_i}) - \nabla \cdot (\boldsymbol{D_i} \cdot \nabla \boldsymbol{c_i}) = \boldsymbol{S_{c_i}} + \boldsymbol{S_i}, \qquad (3.70)$$

where i represents the chemical species HF and H<sub>2</sub>SiF<sub>6</sub>. The two-step operator splitting approach divides the problem into two separate operators: convective-diffusion transport and sources. This allows for independent treatment of these operators in the numerical solution process.

$$\begin{cases} \partial_t \boldsymbol{c}_i + \nabla \cdot (\boldsymbol{v} \cdot \boldsymbol{c}_i) - \nabla \cdot (\boldsymbol{D}_i \cdot \nabla \boldsymbol{c}_i) = \boldsymbol{0}, \\ \frac{d \boldsymbol{c}_i}{dt} = \boldsymbol{S}_{\boldsymbol{c}_i} + \boldsymbol{S}_i. \end{cases}$$
(3.71)

We observe that the problem is now divided into an operator associated with a hyperbolic-elliptic partial differential equation (PDE) and an operator related to an ordinary differential equation (ODE). These two equations can be solved using the Taylor-Galerkin algorithm and the Runge–Kutta (RK) algorithm, respectively. It is important to note that the initial condition for the first PDE is the initial condition of the problem, while the initial condition for the second ODE correspons to the updated solution obtained

from solving the first PDE. The detailed discretization of these equations can be found in Appendix A.3.2.

The iterative procedure from time step  $t_n$  to  $t_{n+1}$  are given in the Table 3.1 Algorithm 3-1.

TABLE 3.1: Algorithm 3-1: Reactive-transport chemo-hydromechanical phase field problem

#### Algorithm 2: Reactive-transport chemo-hydro-mechanical phase field problem

**1**: For each time step  $t^n$ Step 1: **2**: Bound the phase field  $\phi$  in [0,1]. **3**: Solve u/p poroelastic and flow coupled  $\triangleright$  Solve Eqs. (3.14), (3.48)-1. system monolithically. 4: Set  $(p^{n+1}, \boldsymbol{u}^{n+1}) \leftarrow (p^n, \boldsymbol{u}^n)$ , iteration step  $k + 1 \leftarrow$  iteration step k. **Step 2: 5**: Solve phase field  $\phi$ .  $\triangleright$  Solve Eq. (3.48)-2. Step 3: **6**: Solve acid reactive-transport for HF,  $\triangleright$  Solve Eqs. (3.41), (3.42).  $H_2SiF_6$ . Step 4: 7: Solve fast-reacting mineral, slow-reacting  $\triangleright$  Solve Eqs. (3.38), (3.39), (3.40). mineral, and silica gel volume fraction. If convergence: 8: Update  $(\phi^{n+1}, c_{\text{HF}}^{n+1}, c_{\text{H}_2\text{SiF}_6}^{n+1}, c_{\text{M}_1}^{n+1}, c_{\text{M}_2}^{n+1})$  $\begin{aligned} c_{\mathrm{M}_3}^{n+1}) &\leftarrow (\phi^n,\,c_{\mathrm{HF}}^n,\,c_{\mathrm{H_2SiF_6}}^n,\,c_{\mathrm{M}_1}^n,\,c_{\mathrm{M}_2}^n,\,c_{\mathrm{M}_3}^n). \\ \mathbf{9}: \text{ Increment time step } t^n \to t^{n+1}. \end{aligned}$ If non-convergence: 10: Repeat Step 1 to Step 4, iteration step  $k \leftarrow \text{iteration step } k + 1.$ 

## **3.8** Numerical examples

In this section, we present three sets of numerical examples to demonstrate the capabilities of our model from different perspectives. All simulations are performed on two-dimensional problems at the centimeter scale. The gravitational effect is neglected in all cases. In the first example, we revisit the classical unit slit cracking in saturated porous media and compare our results with the findings of Miehe et al. (2010b). Next, we simulate the fracture evolution induced by pure mechanical and chemical degradation. This example showcases the chemo-mechanical coupled effects that arise when the porous media are immersed in a reactive fluid environment, similar to reservoir conditions. We investigate the interaction between mechanical deformation, chemical degradation, and crack evolution, providing insights into the complex behaviour of porous media subjected to multi-physical processes. In the second example, we simulate pressurized injection in a single crack, which is defined by the phase-field parameter. We compare the crack opening and pressure distribution obtained from our numerical simulations with analytical solutions. We also extend the study from pure water-driven cracking to acid fluid-driven cracking. This example enables us to evaluate the accuracy of our model in capturing the poroelastic behaviour of fractures and to verify its predictive capabilities, particularly in terms of both hydraulic and chemical fracturing effects. Finally, we present a core-flooding benchmark, which involves the concentration of acid fluids and changes in porosity. We further simulate the propagation of two cracks induced by the hydraulic injection of reactive fluid into pre-existing flaws. This example comprehensively considers all the factors discussed in our study, including hydraulic, mechanical, and chemical influences on crack propagation. It offers a thorough evaluation of our model's capability to capture the coupled interactions among these factors and their influence on the evolution of fractures. Overall, these three examples showcase the versatility and applicability of our model in simulating various chemo-mechanical processes in porous media.

## 3.8.1 Case 1: Single crack and chemical degradation

The first example involves a square plate measuring 2.0 mm × 2.0 mm with a horizontal crack located in the center. The crack has a length of 1.0 mm and is treated as a closed crack, with its boundary considered a free boundary. The geometric configuration of the specimen, including boundary conditions, dimensions, and mesh refinement, is depicted in Figure 3.5. In this example, we apply a vertically distributed displacement rate to the top edge of the plate while fixing the bottom edge. The applied displacement increases linearly with time according to the function  $u(t) = 10^{-5} \times t$ . Since the main focus of this example is to illustrate the effect of chemical degradation on fracture propagation, we only present the porosity alteration rate. The geochemistry model used in this example is validated with a benchmark in the example of Section 3.8.3.



FIGURE 3.5: Schematic of geometry, mesh refinement, and boundary conditions for the tension problem.

Parameter	Description [Unit]	Value
$\rho_s$	Intrinsic solid mass density $[kg/m^3]$	2700
E	Elastic modulus of solid skeleton [GPa]	210
v	Poisson's ratio of solid skeleton $[-]$	0.3
$G_c$	Critical energy release rate [kN/m]	2.7
$l_0$	Length scale [mm]	0.015
$n_0$	Reference porosity [-]	0.3
r	Experimental reaction constant $[-]$	10
$h_e$	Minimum element size [mm]	0.004

TABLE 3.2: Material properties of the tension problem.

We begin by verifying the classical unit slit problem under tension applied to the top surface. This problem serves as a benchmark to validate the accuracy of our model. Next, we simulate the nucleation and propagation of a crack starting from a pre-existing central crack. This example allows us to study crack evolution and its interaction with the surrounding material. The material parameters used in these simulations are provided in Table 3.2.



FIGURE 3.6: Load-displacement curve of the single-phasic solid subjected to tension.

We assess the model's capability to simulate chemical effects by examining scenarios where the porosity increment,  $\Delta n$ , is 1%, 5%, and 10% of the initial values. The load-displacement relations along the  $x_2$  direction for the top surface of the specimen are presented in Figures 3.6 and 3.7. The simulation results are compared with those of Miehe et al. (2010b) for the case of cracking in a single solid phase. Our model demonstrates a similar trend and provides results closely aligned with the referenced work. Next, we investigate the behaviour of a chemically degraded solid by simulating the load-displacement relations. Figure 3.7 shows that the solid's mechanical performance is weakened overall. As the porosity alteration (increment) increases, the peak load of the specimen decreases while the corresponding displacement increases. When the specimen is completely broken, the chemically degraded porous medium exhibits distinct tensile properties compared to the cracking process of non-degraded porous media. To demonstrate crack nucleation, propagation, and damage, we select a porosity alteration of 10% as an example. The corresponding crack evolution and displacement profiles are depicted in Figures 3.8 and 3.9, respectively.

We further analyze the impact of degradation on the crack and the reservoir domain. Two cross-sectional areas, labelled as a - a' and b - b', are extracted from the schematic in Figure 3.5 to depict the evolution of the phase field value at time steps 965, 1000, 1035, and 1070 respectively. Figure 3.10 illustrates that the area a - a' exhibits clear



FIGURE 3.7: Load-displacement curve of the chemically degraded solid subjected to tension. The chemically degraded by porosity alterations are 1%, 5%, and 10% of the reference porosity.



FIGURE 3.8: Crack evolution patterns of the degraded solid (10% porosity altered) at the displacement of u = 9.56 mm, u = 10.0 mm, u = 10.30 mm, and u = 10.70 mm.



FIGURE 3.9: Displacement ( $x_2$  direction) evolution patterns of the degraded solid (10% porosity altered) at the displacement of u = 9.56 mm, u = 10.0 mm, u = 10.30 mm, and u = 10.70 mm.

evolution of the phase field. It is observed that after the nucleation of cracks, chemical degradation accelerates the cracking process. Furthermore, when comparing the mutually perpendicular areas a - a' and b - b', we observe that no crack nucleation is induced by chemical degradation in the perpendicular area b - b'. Therefore, while chemical degradation can accelerate local crack propagation processes due to crack tip effects, it does not induce the nucleation of cracks around the main crack. Although the chemical degradation in this example assumes homogeneous weakening, the nucleation, propagation, and damage of the crack still exhibit anisotropic behaviour.



FIGURE 3.10: Evolution of the phase-filed values along lines of a - a' and b - b' at the time step 965s, 1000s, 1035s, and 1070s, respectively. A, B, C, and D represents degraded rate of the porous media at 0%, 1%, 5%, and 10%.

### 3.8.2 Case 2: Pressurized injection in a single pre-existing crack

We now proceed to verify the coupling between fluid flow and fracture propagation. Accurately comparing fracture propagation with existing closed experimental results is challenging because the precise measurement of fracture permeability remains a formidable task. Instead, we conduct a verification similar to the work by Bourdin et al. (2012) to compare against the theoretical critical pressure required for fracture propagation to occur.

The verification is conducted against the well-known closed-form formulations derived by Sneddon and Lowengrub (1969) for a two-dimensional line crack aperture, referred to as the crack opening displacement (COD) under internal crack pressure p. It is important to note that the fracture aperture in this context is a static fracture, meaning that neither fluid flow nor fracture propagation is considered. The analytical solution assumes a half-length fracture pressurized with constant (net) pressure. The initial configuration of the domain is shown in Figure 3.11, where a square domain  $\Omega = [-1, 1] \times [-1, 1]$  contains a line crack  $\Gamma_0 = [-a, a]$ . We assign a value of a = 0.5 for the crack length. To conduct the numerical test, we extract a unit volume of the elastic media and consider a quarter of it, as depicted in Figure 3.11, where the displacement and pore pressure boundaries are also illustrated.



FIGURE 3.11: Schematic of geometry and boundary conditions for the pressurized injection problem.

For the internally pressurized fracture, Sneddon and Lowengrub (1969) proposed an analytical solutions for the opening of the fracture between [-a, a], which is:

$$u^{+}(x_{1},0) = \frac{2pa}{E'} \left(1 - \frac{x_{1}^{2}}{a^{2}}\right)^{\frac{1}{2}},$$
(3.72)

with  $E' = E(1 - \nu^2)$  being the plane strain elastic modulus, p is the injection pressure, and  $u^+$  illustrates the opening displacement along the crack,  $x_1$  denotes the point on the crack.

Since we know  $u^+(x_1, 0) = u^-(x_1, 0)$ , and the fracture volume is  $V = \frac{2\pi p a^2}{E'}$ . The strain energy is:

$$E_p = -\frac{1}{2}pV = -\frac{\pi p^2 a^2}{E'},$$
(3.73)

In this case, we follow the concept of Griffith's criteria to calculate the critical fluid pressure to trigger crack as:

$$G_{c} = -\frac{\partial E_{p}}{\partial (2a)} = \frac{\pi p^{2}a}{E'}; p_{c} = (\frac{E'G_{c}}{\pi a})^{\frac{1}{2}}.$$
(3.74)

in which the critical crack energy release rate and the critical fluid pressure for crack propagation are obtained.

The analytical solution for the steady-state pressure profile around the fracture (along the crack tip to the boundary of the domain) with the radial analytical solution for well-bore flow is given by,

$$p = (p_0 - p_w) \frac{\ln(\frac{r}{r_w})}{\ln(\frac{r_0}{r_w})} + p_0, \qquad (3.75)$$

where  $p_0$  is the initial reservoir pressure.  $p_w$  is the reservoir pressure.  $r_0$  is drainage radii which is from crack tip to the boundary of the domain.  $r_w$  is well-bore radius.

We provide the simulation parameters in Table 3.3, and the remaining details of the simulation are illustrated below. The mesh around the pre-existing crack is refined using two different refinement levels. The minimum size of the coarse mesh is  $h_e = 0.004$  m, while the minimum size of the fine mesh is  $h_e = 0.0007$  m. The total number of time steps is set to 2000 with a time increment of  $\Delta t = 1$ s. It is important to note that we can calculate the fracture permeability using Eq. (3.57), but the permeability of fracture flow here is formulated using the cubic law and is set as a constant (significantly lower). This choice is made to approximate the simplified conditions of the analytical solutions for the purpose of comparison.

The computed phase field and pore pressure distributions are presented in Figure 3.12. We consider a general scenario of pressurized injection in a pre-existing crack, where the injection pressure p is varied as 3, 6, 9, 12, and 15 MPa. Figure 3.12 shows the evolution of the fracture and the redistribution of fluid pressure along the propagating fracture. Since the injection pressure is determined by Eq. (3.74), the width of the crack does not show significant variation. As previously mentioned, to capture the process of hydraulic fracturing, we have set a much lower permeability for the porous media surrounding the reservoir, while fracture permeability is much higher. Consequently, we observe that maximum pressure occurs inside the fracture, and pressure diffusion is mainly limited to the immediate vicinity of the fracture. Therefore, fluid transport takes place along the fracture, leading to rapid filling of the fracture. This behaviour is consistent with

expectations in hydraulic fracturing engineering. We then establish an acid injection scenario for unit silt, building on the previously modeled pressurized injection of pure water into a single pre-existing crack, as shown in Figure 3.13. We designate the entire computational domain of the porous media to consist of a fast-reacting mineral, such as calcite. The acid chemical reaction is confined to the initial phase of the simulation, specifically occurring during the first time step, as described by the reaction equation Eq. (3.32). Alteration of the porous media is considered by capturing the evolution of the concentration of the chemical species HF, as described in Eq. (3.41). We set the concentration boundary condition at the pre-existing crack edge to a constant value of  $1620 \text{ mol/m}^3$ , while the remaining boundaries are set to zero. The remaining parameters for the chemical species of HF used in the simulation can be found in Table 3.3. We note that the extended pressurized injection example considers the simplified reactive flow transport inside the crack. We primarily confirm the interactions between solid medium and reactive fluid and further compare the phase field evolution to study the feasibility of mechanical crack propagation assisted by chemical reactions. To make the computation more stable, after the breakdown of the rock, the injection rate gradually decreases during fracture growth.



FIGURE 3.12: Phase field and the corresponding pore pressure evolution under pure water pressurized injection.

Quantitative comparisons and analyses are performed for the pressurized injection



FIGURE 3.13: Phase field evolution under acid pressurized injection.

scenarios. We compare the COD obtained from our simulations with the analytical solutions under different pressure injection values. Additionally, we analyze the pressure distribution from the fracture tip to the end of the domain under an injection pressure of 15 MPa. We also extend the scenario from pure water hydraulic fracturing to acid fluid hydraulic fracturing, where the injection rate is a monotonically decreasing function. The loads are applied in two steps: During the first step ( $0 \le t \le 15$  s), the pressure and concentration boundaries are applied as a constant function of 15 MPa, and zero boundaries are applied for displacement, pressure, and concentration. In the second step (t>15 s), the pressure and concentration decrease from 15 MPa according to the function ( $15 - 0.1 \times t$ ) until the propagation of the crack reaches the edge of the domain. The comparison results are presented in Figure 3.14 and Figure 3.15.

Overall, the simulation results demonstrate that the numerical model can accurately capture the COD and pressure around the crack. The numerical analysis shows good agreement with analytical solutions, although there are slight differences. It is worth noting that as the injection pressure increases, the numerical solution values tend to be slightly higher than those of the analytical solutions. This discrepancy can be attributed to a fundamental assumption made in the analytical solutions, which assumes a sharp crack shape with a fully impermeable crack surface. In our study, we consider the strong coupling effects between the solid and the pore fluid, leading to the observed differences between the numerical model and the analytical solutions. The strong coupling effects here emphasize the relationships between the solid displacement and the pore pressure. A common approach in hydraulic fracturing modelling is to sequentially couple the phase field with the solid displacement and the pore pressure, without considering the strong interactions between solid displacement and pore pressure in geomaterials (Zhou et al., 2018; Lee et al., 2017; Ehlers and Luo, 2017). However, in our framework, we attempt to couple the solid displacement and pore pressure first and then update the phase field. We note that these slight differences are contrary to the findings of Zhou et al. (2018), who did not account for the strong coupling effects between the solid and pore fluid. The numerical results also indicate a nearly constant pressure within the fracture (< 0.01 m left of Figure 3.15), followed by a logarithmic pressure decrease to zero at 0.5 m, which aligns well with analytical solutions. As a result, the model accurately captures the leak-off in the porous media.



FIGURE 3.14: Comparison result for crack opening displacement (COD) along the preexisting crack between numerical solutions and analytical solutions.

In addition, the phase field evolution under acid-pressurized injection exhibits a similar distribution to that of pure water-pressurized injection. Overall, the porous medium breaks down under the injected pressure of 15 MPa. However, the computational process becomes unstable due to the property changes of the porous media at every iteration. To address this, we refine the time step from 1 s to 0.1 s and decrease the injection rate simultaneously. The dashed curve in Figure 3.14 illustrates that the crack growth under acid-pressurized injection occurs more rapidly than under pure water-pressurized injection. A lower excess pore pressure for chemo-assisted fracturing is observed in the extension of Case 2. It is important to emphasize that the phase field contour in Figure 3.12(b) appears imperfect due to the porosity alterations. Theoretically, this discrepancy arises from a time-scale problem between solid displacement, stress, and



FIGURE 3.15: Comparison result for fluid pressure from the tip of preexisting crack to the end of domain under the injected pressure 15 MPa.

chemical reactions, which is a topic for future investigation.

Parameter	Description [Unit]	Value
$\rho_s$	Intrinsic solid mass density $[kg/m^3]$	2700
$ ho_{por}$	Intrinsic porous fluid mass density	1000
	$[\text{kg/m}^3]$	
$ ho_f$	Intrinsic fracture fluid mass density	1000
	$[\mathrm{kg/m^3}]$	
$\kappa_{por}$	Intrinsic reference porous permeability	$1.25\times10^{-16}$
	$[m^2]$	
$\kappa_f$	Intrinsic reference fracture permeability	$1.0  imes 10^{-5}$
	$[m^2]$	
$ u_{por}$	Intrinsic porous fluid dynamic viscosity	$1.0  imes 10^{-6}$
	$[kPa \cdot s]$	
$ u_f$	Intrinsic fracture fluid dynamic	$1.0 \times 10^{-6}$
	viscosity $[kPa \cdot s]$	
$c_1$	Threshold value for porous reservoir [-]	0.4
$c_2$	Threshold value for fracture $[-]$	1.0
$q_R$	Source injection in porous reservoir	0.0
	$[{ m kg/m^3 \cdot s}]$	
$q_f$	Source injection in fracture $[kg/m^3 \cdot s]$	0.0
E	Elastic modulus of solid skeleton [GPa]	210
v	Poisson's ratio of solid skeleton $[-]$	0.2
$G_c$	Critical energy release rate [kN/m]	2.7
$l_0$	Length scale [mm]	0.015
$n_0$	Reference porosity $[-]$	0.3
r	Experimental reaction $constant[-]$	10
$h_e$	Minimum element size[mm]	0.004

TABLE 3.3: Material properties of the pressurized injection problem.

# 3.8.3 Case 3: Fracture propagation and intersection under acid reactive fluid source injection

A benchmark test for multi-mineral dissolution/precipitation is conducted to verify the capability of capturing mass exchange between fluid and solid in a simulation. We perform a coreflooding numerical test and compare the numerical results with the acidizing experimental data published by Hill et al. (1981); Li et al. (1998). For this simulation, we model a cylindrical core plug with dimensions of 1 inch in diameter and 4 inches in length. The reaction takes place at a temperature of 125 °F (324.82 K), using 212 °F (373.15 K) as the reference temperature for the system. Parameters used in the core flooding benchmark are provided in Table 3.4 and are also utilized in the subsequent acid injection simulation case. When handling multi-mineral categories, we adopt the approach outlined by Xie et al. (2023), assigning 70% wt to fast-reacting minerals and 30% wt to slow-reacting minerals. The kinetic data and parameters used in the simulations are sourced from Li et al. (1998) and Xie et al. (2023).

The comparison results between the numerical simulations and experimental data are presented in Figures 3.16 and 3.17. We analyze the concentration of the key acid species HF obtained from the numerical simulations and compare it with the experimental data under different injection rates. The results exhibit good agreement between the numerical solutions and experimental data, underscoring the accuracy of our simulation. Furthermore, we compare the permeability changes resulting from acid erosion. The permeability change in our model is calculated using the empirical relation given by Eq. (3.52). The comparison demonstrates that the numerical model is capable of reasonably capturing the permeability changes induced by acid erosion, as observed in the experimental data. These analyses collectively validate the reliability and effectiveness of the geochemistry model employed in our simulations for representing the reactivetransport processes in porous media, particularly in the case of sandstone.



FIGURE 3.16: Comparison results for one-dimensional core-flooding between numerical solutions and experimental results. EXP. Data are from Hill et al. (1981); Li et al. (1998).



FIGURE 3.17: Comparison results for permeability changes under different acid injection rates between numerical solutions and experimental results.



FIGURE 3.18: Schematic of geometry, boundary conditions, and mesh for the injection problem.

In the subsequent analysis, we investigate the interaction of two chemically and hydraulically induced cracks by injecting acid fluid into the two pre-existing notches. The geometric configuration is shown in Figure 3.18, where we have a rectangular domain of size  $0.2 \text{ m} \times 0.1 \text{ m}$  with two edge notches of length 0.02 m. The notches are perpendicular to each other and are separated by a distance of 0.01 m.

The propagation of the cracks is initiated by the injection of acid fluid directly into the notches. The parameters for this injection are set at a rate of  $100 \text{ kg/m}^3 \cdot s$ , with an HF acid concentration of 1620 mol/m<sup>3</sup>. Boundary conditions for this simulation include fixed displacements at the external boundaries, signifying an absence of movement, and drainage conditions for fluid boundaries, indicating zero pore pressure and concentration. The solid material within the computational domain is considered a composite of multiple minerals, distributed homogeneously throughout. As highlighted in the core flooding segment, the solid constituents are categorized into three main groups: fast-reacting minerals (such as feldspar, calcite, and siderite), slow-reacting minerals (like quartz and illite), and silica gel. The remaining parameters necessary for the simulation are detailed in Table 3.4. This setup allows for a comprehensive investigation of dual crack propagation under the influence of chemical and hydraulic factors.

Parameter	Description [Unit]	Value
$ ho_{por}$	Intrinsic porous fluid mass density [kg/m <sup>3</sup> ]	1000
$ ho_f$	Intrinsic fracture fluid mass density $[kg/m^3]$	1000
$\kappa_{por}$	Intrinsic reference porous permeability $[m^2]$	$1.25\times 10^{-16}$
$\kappa_{f}$	Intrinsic reference fracture permeability $[m^2]$	$1.0 \times 10^{-5}$
$ u_{por}$	Intrinsic porous fluid dynamic viscosity $[\rm kPa\cdot s]$	$1.0  imes 10^{-6}$
$ u_f$	Intrinsic fracture fluid dynamic viscosity $[\rm kPa\cdot s]$	$1.0 \times 10^{-6}$
$c_1$	Threshold value for porous reservoir $[-]$	0.4
$c_2$	Threshold value for fracture $[-]$	1.0
$q_R$	Source injection in porous reservoir $[kg/m^3 \cdot s]$	0.0
$q_f$	Source injection in fracture $[kg/m^3 \cdot s]$	0.0
$ ho_{sf}$	Intrinsic fast-reacting mineral mass density $[kg/m^3]$	2500
$\rho_{ss}$	Intrinsic slow-reacting mineral mass density $[kg/m^3]$	2650
$ ho_{ssg}$	Intrinsic silica gel mass density $[kg/m^3]$	2100
$C_{0,M_1}$	Initial volume fraction of fast-reacting mineral ${\rm M}_1$ [%]	15
$C_{0,M_2}$	Initial volume fraction of slow-reacting mineral ${\rm M}_2~[\%]$	85

TABLE 3.4: Material properties of the acid reactive fluid injection problem.

TABLE 3.4: Material properties of the acid reactive fluid injection problem (continued)

Parameter	Description [Unit]	Value
$E_1$	Reaction constant of fast-reacting mineral HF-M <sub>1</sub> $[m/s]$	$1.27\times 10^{-1}$
$E_2$	Reaction constant of slow-reacting mineral $HF-M_2$ [m/s]	$2.32\times 10^{-8}$
$E_3$	Reaction constant of fast-reacting mineral $\rm H_2SiF_6\text{-}M_2~[m/s]$	$2.0  imes 10^{-7}$
$E_4$	Reaction constant of slow-reacting mineral $H_2SiF_6-M_2$ [m/s]	$5.0 \times 10^{-5}$
$S_1^{\star}$	Interfacial area of $M_1 \ [m^2/m^3]$	235000
$S_2^{\star}$	Interfacial area of $M_2 \ [m^2/m^3]$	300000
$S_3^{\star}$	Interfacial area of $M_3 \ [m^2/m^3]$	333000
$\beta_1$	Dissolution coefficient of HF-M <sub>1</sub> $[kg/kg]$	0.486
$\beta_2$	Dissolution coefficient of HF-M $_2~\rm [kg/kg]$	0.5
$\beta_3$	Dissolution coefficient of HF-M $_3~\rm [kg/kg]$	0.8
$\beta_4$	Dissolution coefficient of $H_2SiF_6-M_1$ [kg/kg]	2.47
$D_{HF}$	Diffusion coefficient of HF $[m^2/s]$	$5.2 \times 10^{-6}$
$D_{H_2SiF_6}$	Diffusion coefficient of $H_2SiF_6$ [m <sup>2</sup> /s]	$5.2 \times 10^{-6}$
E	Elastic modulus of solid skeleton [GPa]	12.42
v	Poisson's ratio of solid skeleton [-]	0.3
$G_c$	Critical energy release rate [kN/m]	0.02
$l_0$	Length scale [mm]	0.015
$n_0$	Reference porosity [-]	0.3
r	Experimental reaction constant[-]	10
$h_e$	Minimum element size[mm]	0.0007

In the simulation results illustrated in Figure 3.19 (a), we show crack patterns at different time steps (20s, 35s, and 75s) to visualize the crack nucleation and propagation process. Additionally, Figures 3.19 (b) and (c) illustrate the pore pressure diffusion and displacement magnitude within the domain, respectively. These observations are consistent with the behavior expected in hydraulic fracturing processes, where the injection of fluid triggers a crack propagation, and damage in the porous media. The pressure diffusion and displacement patterns further highlight the dynamic nature of the crack growth and surrounding material deformation (Section 3.8.2). In Figure 3.19 (c), it can be observed that the injected fluid preferentially fills the cracks, dissipating around the diffusion zone between the cracks and the reservoir. This behavior is in line with the tendency of the fluid to follow the path of least resistance and flow into the existing fractures. The displacement magnitude distribution reveals a strain concentration within

the pre-existing cracks. This localized strain highlights the areas of deformation and damage that occur near the cracks due to the applied loads and interactions between the cracks.

In Figures 3.20 (d) and (e), we observe alterations in porosity and permeability rates relative to their reference values  $(\frac{n}{n_0} \text{ and } \frac{k}{k_0})$ , demonstrating the impact of mineral reactions on the porosity and permeability of the porous media. Intensive mass exchange occurs inside the cracks, leading to significant alterations in porosity, reflecting the intensity of the reactions. Our simulations confirm that the dissolution of different minerals impacts the overall mechanical properties of sandstone, supporting the findings from the experimental studies (Hangx, 2005; Hangx et al., 2013).

To better analyze the mass exchange of different mineral categories, we categorize the solid constituents into three groups based on their reactivity. As shown in Figure 3.21 (f), the fast-reacting mineral is the primary constituent undergoing dissolution in this scenario, with a small amount of silica gel appearing inside the fracture, as illustrated in Figure 3.21 (h). The slow-reacting mineral, depicted in Figure 3.21 (g), shows a negligible change within this particular time frame. However, it is crucial to note that slow-reacting minerals may exhibit changes over extended durations due to chemical reactions.



FIGURE 3.19: The simulation results for the phase field, pore pressure, and displacement at time 20s, 35s, and 75s. (a) The phase field evolution; (b) the pore pressure evolution; (c) the displacement magnitude evolution.


FIGURE 3.20: The simulation results for the porosity and permeability alteration rate at time 20s,35s, and 75s, which is referring to the reference porosity and permeability, respectively. (d) The porosity alteration rate; (e) the permeability alteration rate.



FIGURE 3.21: The simulation results for volumetric of the multiminerals. (f) The fast-reacting mineral; (g) the slow-reacting mineral; (h) silica gel.

Finally, we explore the impact of mineral dissolution on crack propagation by analyzing the evolution of crack length and pressure changes within the domain. The findings reveal that material properties significantly influence the effects of mineral dissolution on crack propagation. Figure 3.22 depicts the crack length's progression as acid fluid is injected under various engineering scenarios. We measure and compare the crack length at each time step across these different scenarios. The graph clearly shows that the injection of acid fluid, which triggers mineral dissolution and subsequently weakens the material, and noticeably slows down the crack propagation. In essence, the rate at which cracks propagate is highly susceptible to the chemical degradation caused by mineral dissolution.



FIGURE 3.22: Crack length in sandstone for pure water injection and acid fluid injection cases.

In addition to analyzing crack length evolution, we also investigate the pressure changes around the cracks, as depicted in Figure 3.23. As the two perpendicular cracks develop, we notice that the cracks are driven purely by fluid consistently exhibit higher pressure compared to those driven by acid fluid. This trend aligns with the results presented in Figures 3.19 through Figure 3.21. The heterogeneous chemical reactions occurring near the cracks lead to rapid pressure dissipation in the surrounding area, explaining why the acid fluid-driven cracks require more time to reach the critical energy release rate necessary for propagation. Incorporating both fast-reacting and slow-reacting minerals in our model provides a more accurate characterization of the heterogeneous chemical



FIGURE 3.23: Fluid pressure distribution along the direction A and B of the cross sections of sandstone specimen at times of 1 s, 10 s, 20 s, 30 s, 40 s, 50 s, and 60 s.

reaction process when compared to previous studies that did not differentiate between different mineral categories (e.g., Schuler et al. (2020)). However, in the long-term analysis, we reach a similar conclusion to their study.

These findings underscore the critical importance of considering geochemical interactions in geological systems, especially in environments where acid engineering is employed. A comprehensive understanding of the interconnected processes between fluid flow, chemical reactions, and mechanical deformation is essential for accurately predicting fracture behavior and devising effective engineering strategies in such challenging environments.

## 3.9 Summary

This study establishes a computational framework utilizing the phase field approach to capture the coupled chemo-hydro-mechanical interactions within brittle porous media. We acknowledge the strong interdependence between solid displacement and pore pressure while integrating chemical processes that account for acid-mineral reactions.

The geochemistry models employed enable precise interactions between fluid and solid, ensuring an accurate mass exchange and constitutive responses. Such detailed representation of porosity enhances the reliability of crack propagation predictions. Our computational model's mechanical response derives from chemical degradation parameters and a weakened elastic modulus that is influenced by the comprehensive interplay of fluid transport and solid crack propagation.

Moreover, the phase field serves as an effective and efficient indicator, unifying the governing equations for pore pressure diffusion and acid chemical species transport. This method ensures a smooth transition of material properties from sharp interfaces to diffusion zones.

We recognize that more accurate calculations of chemical influences on mechanical responses are essential for a profound impact on poromechanics problems involving mass exchange between fluid and solid. Our future research endeavors will concentrate on developing a more intricate constitutive description of the reactive surface of solids, considering the chemical reaction rate. These investigations are currently ongoing.

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# Chapter 4

# Thermodynamics-based constitutive modeling of chemically-induced grain degradation for cohesive granular materials

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# Thermodynamics-based constitutive modeling of chemically-induced grain degradation for cohesive granular materials

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# Abstract

This paper focuses on studying the chemically-induced degradation of grains and bonds in cohesive granular materials, employing a thermodynamically consistent approach. To capture the stiffness degradation and bonding/debonding phenomena in cohesive granular materials, such as granular soils, due to chemo-mechanical coupled influences, this study introduces chemical potential energy, including pore geochemistry and pressure dissolution, into the classical Modified Cam-Clay-type (MCC) model. The study introduces a cross-scale relation to address microscale dissolution at the grain and bond contact. Furthermore, the contact force is determined by an evolving on accumulative particle size distribution, characterized as the probability size distribution density function, due to chemical degradation. Lastly, the paper derives the algorithmic tangent operator for finite element (FE) boundary problem simulations. The study conducts multiple validations and verifications of the proposed model. Evaluations comparing the model's performance with laboratory experiments were carried out. It is concluded that the model successfully explains the macroscopic observations of geomaterial degradation widely observed in geotechnical engineering.

**Keywords:** Constitutive modeling, Thermodynamics, Chemical dissolution, Degradation of grain and bond, Granular materials.

## 4.1 Introduction

Many natural disasters are relevant to chemically-induced weathering, such as landslides (Bogaard et al., 2007; Fan et al., 2017; Baldermann et al., 2021), sinkholes (Kaufmann and Romanov, 2016), and cave collapses (Canakci, 2007; Osborne, 2002). Research on these disasters reveals that the coupling among mechanical, hydrological, and chemical processes, as well as human activities, alters the microstructure features of the geomaterials. The alterations in microstructure can be reflected in macroscopic phenomena, including structural damage and changes in the strength of geomaterials. Most macroscopic phenomena are described using phenomenologically based formulations to represent the macroscopic behaviors of the integrated aggregates. However, microscale processes in the pore volume can generate measurable couplings at the scale of a representative elementary volume (REV). Examples of microscale processes in the pores include pressure dissolution, mechanical compaction, cementation, mineral transformation, sulfate-induced expansion, and so on. However, introducing microscale processes into a macroscale continuum constitutive model is challenging. One challenge is mapping microscale processes to macroscale processes. Another is preserving the microscopic physical meaning of parameters tested from macroscopic experiments.

In this paper, we focus more on the mass exchange description of stiffness degradation and bonding/debonding effects from microscopic mechanisms. We introduce the chemical reactions caused by an aqueous environment subject to pressure dissolution. There are different constitutive models to describe the influences of weakening or strengthening effects on the mechanical behavior from different viewpoints. Buscarnera and Das (2016) started from the Breakage Mechanics Theory and proposed breakage and damage parameters to track changes in the size of grains and bonds. They properly explained the observed geomaterial degradation by reconciling the energetics of the deformation/reaction processes with the evolving geometry of the microstructural attributes. Similar works can be found in the frozen sandy soil (Zhang et al., 2018), saturated natural loess (Fu et al., 2021), and the bonding dissolution for structured soil (Zhang et al., 2022) literature.

To better understand single grain and bond evolution from geometric boundaries, some researchers focused more on the description of the bounding surfaces. Gajo et al. (2015, 2019) explored the evolution of the microscopically geometrical cross-scale area for reactive bond and grain cases, respectively. The relationships linked to porosity and permeability were proposed to keep track of all-important bound-related parameters. Bista et al. (2022) defined the chemo-mechanical coupling mechanisms directly on the intergranular contact, and further simulated on the discrete element framework. Yasuhara et al. (2003) considered grain interpenetration mathematically, and well-predicted longterm rates of change of porosity. They considered pressure solution processes, including grain-contact pressure dissolution, dissolved solute diffusion, and precipitation at the pore walls. However, the upscale method, from the single grain and bond to solid aggregates, is much more complex to implement. A compromise method is to introduce microscopic mechanisms to the macroscopic properties into classical models. There are plenty of models established based on the conventional Modified Cam-Clay (MCC) model. Those models were revised based on the MCC model and considered the soil structural characteristics (Asaoka et al., 2000; Ma ín, 2007; Mendoza and de Farias, 2020).

It is well known that thermodynamics provides a rigorous foundation for deriving constitutive equations, especially for quantifying energy transformations (Houlsby, 1981; Collins and Kelly, 2002; Yan and Li, 2011; Zhang et al., 2022; Viswanath and Das, 2020). In this work, we pay attention to connecting the environmental chemical reactions with the stress field. The potential energy for a system of solid and fluid is a good way to reach the purpose. Pioneer works have been completed via thermodynamics to derive constitutive models to introduce grain degradation or bonding/debonding effects. Houlsby (1981) derived the Modified Cam-Clay model from the thermodynamic method and proposed the changes to the yield locus with the integration of critical state theory, isotropic hardening rule, and associated flow rule. Collins and Kelly (2002) then provided a general framework for the hyperplastic constitutive model based on thermodynamics. Yan and Li (2011) developed a thermodynamically consistent constitutive model and introduced the evolution law of the thermodynamical force. Recently, Chen et al. (2023) established constitutive models by thermodynamics (beyond just the first and second laws) is to derive constitutive equations using the hydrodynamic procedure. Their model was used to predict the chemo-mechanics of poroelastic materials. The model revealed the connection of densities to chemical potentials and pore fluid pressure, and showed

that the latter quantity is governed by both density and osmotic concentration.

This work extends a thermodynamically consistent model to consider both the grain and bond evolution with the derivation from the dissipation function. Different from the previous studies, mass exchange, and pressure dissolution effects are included in thermodynamics. We derive the reaction kinetic rate and introduce it into the dissolutiondependent degradation function to capture both mechanical and chemical effects on constitutive response. Unlike studies on tracking the size changes of a single grain or bond, we integrate all sizes of the solid aggregates and introduce the reaction kinetic rate for every grain and bond to capture its size evolution during chemical reaction processes. The integration is related to a probability density function that is widely accepted to characterize intergranular pore size distribution. We note that stress here is interparticle contact force which is highly relevant to the probability density function ( for a well-distributed particle size curve (Liu et al., 2023)). Therefore, we obtain the contact stress using the cumulative distribution of particle sizes by volume versus the cumulative distribution of particle sizes by mean effective stress for specimens. The stiffness degradation and internal variable of bonding/debonding then can be derived with this consideration. The rest of the mathematical derivations follow a class of the two-invariant stored energy functions appropriate for Cam-Clay-type models. Finally, we also derive the consistent tangential moduli so that the constitutive model can be not only on stress-point simulation but also for FE problems as a constitutive module coupled into complex multiphysical problems.

The paper is structured as follows: We introduce the main aspects of the proposed model from the thermodynamic principles in Section 4.2. The macroscopic and microscopic formulations are both included in this section; Section 4.3 introduces the numerical algorithm to realize the proposed constitutive model in Section 4.2; in Section 4.4, the parametric studies for the proposed model are discussed. The model validations against experimental data are also mentioned in this section. The conclusions and outlook are drawn in Section 4.4.

## 4.2 Methods

In this section, we first introduce the overall framework for the chemically-induced degradation of grains and bonds in granular materials. We define the geomechanical problem in a background statement and then introduce the chemistry and degradation characteristics of the problem. Moreover, we establish a constitutive theory using a

potential energy functional while considering the hyperelasticity and plasticity with the classical modified Cam-Clay model and further introduce the degradation into the corresponding elastic and plastic constituents of the constitutive model.

# 4.2.1 The theoretical framework of chemically-induced degradation of grain and bond

Dissolution of reactive mineral constituents in rock and soil is one of the key reasons for the weathering of geomaterials during long-term interactions with fluid. However, these processes are not easily captured because they involve multiple mineral species and complex microscopic structures. We have reviewed the relevant studies in the Section 4.1 and pointed out the challenges in the characterization of both bond and grain dissolution processes. In this section, we link the grain-size distribution (GSD), and bond-size distribution (BSD) with the dissolution reaction process, and then derive the degradation effects at the constitutive level.

#### 4.2.1.1 Geomechanical background

The dissolution processes for granular material interacting with fluid include the mass dissolution of grains and bonds, as well as the transport of the dissolved mass in the liquid phase. The transport of the dissolved mass is always coupled with solid deformation to capture the alteration of hydraulic conductivity properties, such as permeability and porosity, which further affects the macroscopic stress-strain response. (Meakin and Tartakovsky, 2009; Zuo et al., 2019; Guo and Na, 2024).



FIGURE 4.1: Scheme of grain and bond degradation due to stress dissolution and diffusion mechanisms. (a) Before load on the soil aggregate; (b) After load on the soil aggregate.

The altered mechanical properties not only have a significant influence on fluid transport but also capture the effects of grain and bond degradation via stresses and reactions at the constitutive level. The scheme of the dissolution processes of soil aggregates is shown in Figure 4.1. Let us compare the soil aggregate before and after dissolution about stress and chemical reactions. The basic mechanisms for dissolution-transportation are illustrated in Figure 4.1(b). There are three stages:

- (1) Reactive components in the fluid are transported to the grain-to-grain contact interface, governed by diffusion or advection.
- (2) Pressure dissolution occurs due to the contact force acting on the grain-to-grain contact surface.
- (3) Dissolved mass at the contact is transferred to the adjacent area of the contact via diffusion.

Several models capture the micro-structure-relevant dissolution, such as water film diffusion models (Weyl, 1959; Rutter and Elliott, 1976; Tada et al., 1987) and islandchannel models (Shimizu, 1995; Raj and Chyung, 1981; Barber et al., 1990). Shen et al. (2011) analyzed the differences between the two categories of models and concluded that stress can effectively accelerate the dissolution rate. We note that these two phenomena can occur simultaneously with a certain probability but will be dominated by one of them for a specific reactive geomaterial (Tada et al., 1987; Shen et al., 2011).

In this study, we refer to the research work of Pietruszczak et al. (2006). The chemical reaction for pressure dissolution includes two phases: one is the very fast dissolution of contacts at the periphery of the interface, and the other is the much slower dissolution/diffusion in the region adjacent to the center of the interface. These processes lead to significant degradation of mechanical properties on the macro-scale, such as bonding degradation (Zhang et al., 2022) and stiffness degradation (Viswanath and Das, 2020), primarily due to a reduction in the effective solid contact area between grains. The reduction effects are characterized by a micro-scale description from a chemical reaction perspective. Cross-scale formulations are proposed to link the micro-scale description with the macro-scale degradation phenomenon. Micro- and macro-descriptions of single grain/bond chemical dissolution induced by chemo-mechanical effects and granular aggregate degradation are sequentially addressed in the respective subsections.

#### 4.2.1.2 Kinetic rate laws for geochemical reactions on geomechanical response

We consider a dynamic mechanical system that is driven by chemical potential energy during the mass and energy interactions. According to the definition of potential energy, we express Gibbs potential energy G as an extensive property adding the Helmholtz free energy and work by the fluid pressure (Greiner et al., 2012).

$$G = \Psi + pv \tag{4.1}$$

where  $\Psi$  is the Helmholtz free energy, which is simplified and expressed as the solid strain energy; p is the fluid pressure working on the solid; v is the partial molar volume of the solid phase.

Since we consider the stress and strain changes for the geomaterial undergoing the dissolution processes, the change of the Gibbs potential energy  $\Delta G$  reads:

$$G^{solid} = \Psi^{solid} + \sigma_n v^{solid} \tag{4.2}$$

$$G^{liquid} = \Psi^{liquid} + pv^{liquid} \tag{4.3}$$

$$\Delta G = (\Psi^{liquid} - \Psi^{solid}) + (pv^{liquid} - \sigma_n v^{solid}) = p(v^{liquid} - v^{solid}) - (\sigma_n - p)v^{solid}$$

$$(4.4)$$

We denote the potential energy stored in the solid and fluid as *solid* and *liquid*, respectively. In Eq. (4.4), we consider the local equilibrium of strain energy, which actually will be considered during a global time step during the loading process. We refer to the thermodynamical models on mineral solubility and ignore the molar volumetric changes between solid and liquid phases (Li et al., 2018). Thus, Gibbs potential energy is reduced further as:

$$\Delta G = -(\sigma_n - p)v^{solid} = -\sigma'_n v^{solid} \tag{4.5}$$

If we refer to the thermodynamic solubility model that captures the equilibrium processes, the chemical potential of dissolution is locally conservative which is equal to the previous external changes of the total potential energy. In this case, we develop the conservative law as below:

$$\Delta G = -\sigma'_n v^{solid} = RTln(\frac{a^{liquid}}{a^{solid}}) \tag{4.6}$$

where  $a^{\beta}$ ,  $a^{\alpha}$  are activity of liquid and solid phase, respectively; R is the universal

gas constant; T is Kelvin temperature. Here, the right side of the term refers to the thermodynamic activity-activity model, which describes the non-ideal behavior of components in mixtures, such as mineral dissolution, by relating their activities to actual concentrations through activity coefficients (Li and Duan, 2011). Therefore, we express the activity of the solid phase considering the external stresses acting on the system as below:

$$a^{solid} = a^{liquid} e^{\frac{\sigma'_n v^{solid}}{RT}}$$
(4.7)

Consequently, we employ transition state theory, noting that a reaction occurs when it exceeds the activation energy. (Lasaga, 1981a,b; Lasaga and Rye, 1993). The above activity relations characterize the Gibbs energy changes before and after reactions. So, we express the dynamic dissolution reaction rate K as:

$$K = \kappa s \Delta G = \kappa s (\Delta G^{\Theta} + RT ln \prod^{i=liquid,solid} a^{i})$$
(4.8)

where  $\kappa$  is reaction constant; *s* is the reaction size;  $\Delta G^{\Theta}$  is the changes of Gibbs energy under standard reference conditions;  $\prod^{i=\alpha,\beta} a^i$  is activity product of dissolved minerals, *i* is for liquid or solid phase. If we introduce the activity formula in Eq. (4.7) and the equilibrium state of dissolution  $K^{eq}$  into Eq. (4.8), we have:

$$K = \kappa s \Delta G = \kappa s (\Delta G^{\Theta} + RTln \frac{Q}{e^{\frac{\sigma'_n v^{solid}}{RT}}}) = \kappa s (\Delta G^{\Theta} + RTln Q - \sigma'_n v^{solid})$$
$$= \kappa s (\Delta G^{\Theta} + RTln K^{eq} + RTln \frac{Q}{K^{eq}} - \sigma'_n v^{solid}) = \kappa s (RTln \frac{Q}{K^{eq}} - \sigma'_n v^{solid}) \quad (4.9)$$

where we introduce the equilibrium state of Gibbs changes, that is  $\Delta G^{\Theta} + RT ln K^{eq} = 0$ , and  $K^{eq}$  is a equilibrium state associated with the temperature T and pressure p conditions for a specific mineral.

#### 4.2.1.3 dissolution-dependent degradation for bonds and grains

The significant degradation of the mechanical properties of granular geomaterials is primarily attributed to the dissolution of the effective solid contact area, including grain contacts and bonds connecting grains. We consider two key mechanisms indicated by experimental evidence. One is the fast stage, which is the rapid propagation of the dissolution front from the periphery of the contact interface; the other is the second stage, which is the slow dissolution and diffusion of the dissolved material in the region adjacent to the center of the contact interface. Therefore, the exponential formulation from Pietruszczak et al. (2006) is adopted to characterize the progressive degradation of both stages, which is governed by:

$$\dot{\phi}^{chem} = 1 - \alpha e^{-\dot{\xi}\beta_1} - (1 - \alpha)e^{-\dot{\xi}\beta_2} \tag{4.10}$$

where  $\phi^{chem}$  is a degradation parameter, and  $\alpha$  is the weight factor for these two mechanisms. The experimental results revealed that the principal mechanism governing the degradation is the fast stage (Homand, 2000). We follow the suggestion from Pietruszczak et al. (2006) that  $\alpha$  is expected to be in the range of 0.8-0.9.  $\beta_1$  and  $\beta_2$  are material parameters, respectively.  $\xi$  is the solid mass removal parameter from the system, which can be linked with the kinetic law in Section 4.2.1.2. We then introduce the degradation function  $\phi$  in Eq. (4.10) to describe the degradation effect on mechanical properties, which includes elastic energy and internal variables such as hardening law evolution, in Section 4.2.2. We depict the evolution of chemical degradation with increasing dissolution rates under different  $\alpha$  values in Figure 4.2. The material parameters are  $\beta_1 = 20000$  [1/day] and  $\beta_2 = 0.1$  [1/day].



FIGURE 4.2: Degradation function evolution with the dissolution rate under assigned geomaterial parameters.

In the following context, we connect kinetic laws for geochemical reactions with dissolution-dependent degradation. We know that stiffness in granular materials varies with grain mineralogy, bond mineralogy, grain-size distribution (GSD), and bond-size distribution (BSD), void ratio, confining pressure, and contact force. For simplicity in the continuum mechanics approach to dealing with this complex problem, we employ the probability density function of (bond and grain) size distribution to characterize the evolution of GSD and BSD. In this way, the degradation of grain and bond stiffness can be expressed as an evolving probability density function. We note that mass removal is connected to the evolving probability density function.

We first define the chemical variable  $\xi$  to describe the measurement of mass dissolution of the mineral that softens the material.

$$\dot{\xi} = \frac{d\xi}{dt} = \frac{dM_{diss}}{M_0 dt} \tag{4.11}$$

The initial mass  $M_0$  and dissolution of mass with time  $\frac{dM_{diss}}{dt}$  are then connected with GSD and BSD as follows:

$$M_0 = \int_{s_m}^{s_M} s \cdot g(s) ds \tag{4.12}$$

$$\frac{dM_{diss}}{dt} = \int_{s_m}^{s_M} K \cdot g(s,\xi) ds \tag{4.13}$$

Here, we assume the probability density function is a function of mass removal and size. The probability density function is determined by (Buscarnera and Das, 2016):

$$g(s,\xi) = \frac{(3-\beta) \cdot s^{2-\beta}}{s_M(\xi)^{(3-\beta)} - s_m(\xi)^{(3-\beta)}}$$
(4.14)

where  $\beta$  is a material parameter;  $s_M(\xi)$  and  $s_m(\xi)$  are the evolved maximum and minimum reaction (grain or bond) sizes. We can further define them as follows:

$$s_M(\xi) = s_{M0}(1-\xi)^{\frac{1}{m}} \tag{4.15}$$

$$s_m(\xi) = s_{m0}(1-\xi)^{\frac{1}{m}} \tag{4.16}$$

where m is a material parameter that controls how the shape of spherical particles dissolves over time under certain conditions. We follow the assumption of Buscarnera (2012) that a homothetic dissolution of spherical grains sets m = 3.

#### 4.2.2 Constitutive formulations

In this section, we develop a reaction-dependent constitutive model for a cemented granular geomaterial. We derive the explicit expressions of the Helmholtz free energy and dissipation function, which are used to model the elasticity and the evolution of internal variables in the cemented assemblies.

#### 4.2.2.1 Potential energy function

We follow the classical thermodynamics formalism for a Representative Elementary Volume (REV) of the cemented granular geomaterial. With the external strain rate applied to the boundary of a REV, the volume-specific Helmholtz free energy  $\dot{\Psi}$  describes the energy stored in the cemented granular geomaterial. The total volume-specific energy dissipation rate  $\mathcal{D}^p$  is given by Eq. (4.17) according to the first and second laws of thermodynamics under isothermal conditions (Collins and Hilder, 2002; Collins and Kelly, 2002).

$$\boldsymbol{\sigma}: \dot{\boldsymbol{\epsilon}} - \dot{\Psi} = \mathcal{D}^p \ge 0 \tag{4.17}$$

where  $\dot{\epsilon}$  is the strain rate tensor applied on the boundary of the REV, and  $\sigma$  is the corresponding stress tensor. The volume-specific Helmholtz free energy is a state function with the elastic strain rate and plastic strain rate as independent variables. Thus, we further separate  $\dot{\Psi}$  into elastic free energy  $\dot{\Psi}^e$  and plastic free energy  $\dot{\Psi}^p$ . In our model, we select the Modified Cam-Clay (MCC) model to provide the specific formulations of Helmholtz free energy and energy dissipation. Unlike the conventional MCC framework, the problem we consider is coupled between microstructural alteration and pore fluid chemistry. Therefore, we first derive the stiffness degradation for the energy function in a general way and revise the elastic and plastic energy functions for the MCC model accordingly.

The Helmholtz free energy  $\Psi$  stored in solid aggregates can be calculated using the statistical average method, which involves integrating the relationship  $(\psi(\boldsymbol{\epsilon}, s) \cdot g(s, \xi))$  over the particle size distribution. Here, Helmholtz free energy stored in a single particle is denoted as  $\psi(\boldsymbol{\epsilon}, s)$ , which is approximated by the particle size ratio to a reference particle size with the reference energy; i.e.,  $\psi(\boldsymbol{\epsilon}, s) = (\frac{s}{s_r})^n \psi_r$ , where *n* is a proportional parameter, typically set to 2.0 (Einav, 2007). In this case, we integrate the Helmholtz free energy as follows:

$$\Psi = \int_{s_m}^{s_M} \psi(\boldsymbol{\epsilon}, s) \cdot g(s, \xi) ds \tag{4.18}$$

The reference particle size can then be obtained with the previous approximation as:

$$s_r = \left[\int_{s_{m0}}^{s_{M0}} s^n \cdot g(s)\right]^{\frac{1}{n}}$$
(4.19)

If we now substitute the corresponding definitions in Eqs. (4.10),  $(4.11)\sim(4.16)$ , and (4.18) into Eq. (4.17), the Helmholtz free energy in REV can be simplified as,

$$\Psi = (1 - \xi)^{\frac{2}{3}} \psi_r \approx (1 - \phi)^{\frac{2}{3}} \psi_r \tag{4.20}$$

We note that Eq. (4.20) derives from power-law scaling. This simplified equation is initially associated with the mass dissolution of the mineral  $\xi$ . To reflect the physical implications, we approximate the effects of mass removal of  $\xi$  using the damage parameter  $\phi$ .

#### 4.2.2.2 Hyperelasticity

In the true stress space, we assume the material behavior is isotropic, undergoing small strains. Solid grains are assumed to be incompressible and uncrushable. In this case, we propose the yield function follows the lines of an existing approach for bonded geomaterials. However, we enhance the physical meaning of parameters of isotropic tensile and compressive strength relevant to chemical reactions and pressure dissolution. The corresponding macroscopic parameters are defined in the yield function as follows:

$$\begin{cases} \mathcal{F} = \mathcal{F}(p, q, p_c, p_u) = \frac{q^2}{\tilde{M}^2} + (p - p_b)[(p - p_b) - p_d] \\ p_d = p_c + p_u \\ p_u = -bp_b \end{cases}$$
(4.21)

where p and q are mean normal and deviatoric stresses invariant.  $p_u$  and  $p_b$  are bondrelated parameters of structure soil.  $p_c$  is the preconsolidation parameter.  $p_d$  is introduced to enhance the compression strength considering the cemented effects on the soil, while  $p_u$  represents the increase of tensile strength. There is evidence that the bond-related parameters  $p_u$ ,  $p_b$  have negative linear relations that is described as a constant b here (Yan and Li, 2011).  $\tilde{M}$  is the revised critical state stress ratio proposed by Collins and Kelly (2002) to transfer the MCC yield surface into a teardrop shape. The introduction of parameter  $\tilde{\alpha}$  provides additional flexibility for better modeling of shear response. So, we follow the definition that  $\tilde{M} = \sqrt{M^2 [\tilde{\alpha} + (1 - \tilde{\alpha})p/\frac{p_d}{2}]}$ , where M is the critical state stress ratio (Yan and Li, 2011). We follow the hyperelasticity theory and derive the Helmholtz energy as (Borja and Tamagnini, 1998):

$$\Psi_r = \tilde{\Psi}(\epsilon_v^e) + \hat{\Psi}(\epsilon_v^e, \epsilon_s^e) \tag{4.22}$$

where  $\tilde{\Psi}(\epsilon_v^e)$  is the stored energy for isotropic loading that is only related to the volumetric strain invariant, while  $\hat{\Psi}(\epsilon_v^e, \epsilon_s^e)$  considers both volumetric and deviatoric invariants. The shear modulus is influenced by volumetric and deviatoric invariants in this study (Borja and Tamagnini, 1998). Consequently, the stored energy expressed by the strain invariants is given by:

$$\begin{cases} \tilde{\Psi}(\epsilon_v^e) = -p_0 \tilde{\kappa} e^{\left(-\frac{\epsilon_v^e - \epsilon_{v0}^e}{\tilde{\kappa}}\right)} \\ \hat{\Psi}(\epsilon_v^e, \epsilon_s^e) = \frac{3}{2} G \epsilon_s^{e2} = \frac{3}{2} [G_0 + \frac{t}{\tilde{\kappa}} \tilde{\Psi}(\epsilon_v^e)] \epsilon_s^{e2} \end{cases}$$
(4.23)

where  $\epsilon_v^e = tr(\boldsymbol{\epsilon}^e)$  is the infinitesimal volumetric strain invariant, and  $\epsilon_s^e = \sqrt{\frac{2}{3}}|\boldsymbol{\gamma}^e|$  is the infinitesimal deviatoric strain invariant.  $\boldsymbol{\epsilon}^e$  is the infinitesimal elastic strain tensor with a deviatoric component  $\boldsymbol{\gamma}^e$ .  $\tilde{\kappa}$  is the elastic compressibility index, and the infinitesimal elastic volumetric strain  $\epsilon_{v0}^e$  is at a mean normal effective stress of  $p_0$ . The elastic modulus varies from a constant term  $G_0$  with the elastic volumetric strain through the constant coefficient t. Clearly, if t = 0, the elasticity model is defined in a decoupled format by a variable elastic bulk modulus and a constant elastic shear modulus.

We then follow the hyperelasticity equation, that are:

$$\begin{cases} \boldsymbol{\sigma} := \frac{\partial \Psi_r(\epsilon_v^e, \epsilon_s^e)}{\partial \boldsymbol{\epsilon}^e} = \frac{\partial \Psi_r(\epsilon_v^e, \epsilon_s^e)}{\partial \epsilon_v^e} \frac{\partial \epsilon_v^e}{\boldsymbol{\epsilon}^e} + \frac{\partial \Psi_r(\epsilon_v^e, \epsilon_s^e)}{\partial \epsilon_s^e} \frac{\partial \epsilon_s^e}{\boldsymbol{\epsilon}^e} \\ p = \frac{\partial \Psi_r(\epsilon_v^e, \epsilon_s^e)}{\partial \epsilon_v^e}; q = \frac{\partial \Psi_r(\epsilon_v^e, \epsilon_s^e)}{\partial \epsilon_s^e}, \\ \frac{\partial \epsilon_v^e}{\boldsymbol{\epsilon}^e} = \mathbf{1}; \frac{\partial \epsilon_s^e}{\boldsymbol{\epsilon}^e} = \sqrt{\frac{2}{3}} \hat{\boldsymbol{n}}. \end{cases}$$
(4.24)

which after combining with Eq. (4.23), we have,

$$\begin{cases} p = p_0 [1 + \frac{3t}{2\tilde{\kappa}} (\epsilon_s^{e2})] e^{\left(-\frac{\epsilon_v^e - \epsilon_{v0}^e}{\tilde{\kappa}}\right)} \\ q = 3 [G_0 - t p_0 e^{\left(-\frac{\epsilon_v^e - \epsilon_{v0}^e}{\tilde{\kappa}}\right)}] \epsilon_s^e \end{cases}$$
(4.25)

This means the elastic strain-stress relationship considering grain size and dissolution effects becomes,

$$\begin{cases} \dot{p} \\ \dot{q} \end{cases} = (1 - \phi)^{\frac{2}{3}} [\boldsymbol{D}^{\boldsymbol{e}}] \begin{cases} \dot{\epsilon}^{\boldsymbol{e}}_{v} \\ \dot{\epsilon}^{\boldsymbol{e}}_{s} \end{cases}$$
 (4.26)

where  $D^e$  is a Hessian matrix for  $\Psi_r$  which can be derived by the following partial differential relations,

$$\begin{bmatrix} \boldsymbol{D}^{e} \end{bmatrix} = \begin{bmatrix} D_{11}^{e} & D_{12}^{e} \\ D_{21}^{e} & D_{22}^{e} \end{bmatrix} = \begin{bmatrix} \partial_{\epsilon_{v}^{e} \epsilon_{v}^{e}}^{2} \Psi_{r} & \partial_{\epsilon_{v}^{e} \epsilon_{s}^{e}}^{2} \Psi_{r} \\ \partial_{\epsilon_{s}^{e} \epsilon_{v}^{e}}^{2} \Psi_{r} & \partial_{\epsilon_{s}^{e} \epsilon_{s}^{e}}^{2} \Psi_{r} \end{bmatrix}$$
(4.27)

The components of matrix  $[D^e]$  are given in Appendix A.6.

#### 4.2.2.3 Internal variable

As we know the plastic volumetric strain and deviatoric strain are used as internal variables characterizing the material fabric. We follow the same idea from the MCC model to propose the hardening law for preconsolidation and cemented pressure accordingly. The hardening law, expressed in terms of the plastic component of volumetric strain, is governed by:

$$\dot{p_c} = -\frac{p_c}{\hat{\lambda} - \tilde{\kappa}} \dot{\epsilon_v^p} \tag{4.28}$$

in which  $\hat{\lambda}$  is the virgin compression index. The linear relationship is employed to relate the content of the cementation. The hardening law for bonding pressure  $p_b$  is expressed as follows (Gai and Sánchez, 2019):

$$\dot{p}_b = a(\dot{\chi}m_c); d\dot{\chi} = -u\chi\sqrt{(\dot{d\epsilon}^p : \dot{d\epsilon}^p)}$$
(4.29)

where  $\chi$  serves as a damage factor regarding the mechanical degradation of cementation during loading.  $m_c$  is the mass content of the initial bonding. a is the scaling constant that relates  $m_c$  with the mechanical contribution of the bonding. u is a constant that defines the damage rate of the mechanical contribution from the bonding. With the experimental evidence of the contributions of volumetric and deviatoric plastic strain rates to bonding destruction (Yan and Li, 2011), we define the hardening law for bonding pressure as follows:

$$\dot{p_b} = a(\chi_0) m_c e^{\left(-u\sqrt{\frac{2(\delta\epsilon_v^p)^2 + 9(\delta\epsilon_s^p)^2}{6}}\right)} = p_{b0} e^{\left(-u\sqrt{\frac{2(\delta\epsilon_v^p)^2 + 9(\delta\epsilon_s^p)^2}{6}}\right)}$$
(4.30)

We also consider the chemical degradation on the bonding pressure. If we follow the beginning effect in Eq. (4.10), we then have:

$$\dot{p_b} = (1 - \dot{\phi}) p_{b0} e^{\left(-u \sqrt{\frac{2(\delta \epsilon_v^p)^2 + 9(\delta \epsilon_s^p)^2}{6}}\right)}$$
(4.31)

#### 4.2.2.4 Degradation of stiffness and internal variable

We have discussed the degradation effects on the grain and bonding in Sections 4.2.2.2 and 4.2.2.3. However, the specific connection related to the idea proposed in Section 4.2.1.3 is still not defined. In this section, we give the mass dissolution relations for the grains and bonds of the REV.

Firstly, the formulation for degradation effects due to grain dissolution is derived. In our study, we consider the grain-contact dissolution due to the compaction of granular aggregates. We reconfigurate the mechanism proposed by Yasuhara et al. (2003). In their model, the single grain-contact series model is proposed, which considers both the contact force effects and geometry evolution of a grain. We simplify the diffusion flux inside of a contact area and precipitation of the surface of the grain as an assigned constant. We then extend the single grain-contact series to a distributed grain domain, i.e.:

$$\frac{dM_{diss}}{M_0 dt} = \frac{3\pi V_m^2 k_+ \rho_g d_c^2}{4RT(\frac{1}{6}\pi s^3)} (\sigma_a - \sigma_c)$$
(4.32)

where  $V_m$  is molar volume of the solid,  $k_+$  is the dissolution rate constant,  $\rho_g$  is the grain density,  $d_c$  is the diameter of the grain-to-grain contacts,  $\frac{1}{6}\pi s^3$  is the volume of grain,  $\sigma_a$  and  $\sigma_c$  are the stress applied at the contact area and critical stress, respectively.

Actually,  $(\sigma_a - \sigma_c)$  is the effective stress applied on the grain-to-grain contacts. We refer to the work of Liu et al. (2023), in which the particle stress in well-graded soil is related to the cumulative distribution of particle sizes. We pick up the percentage passing by volume and percentage contribution to the stress in their work, and regress the linear relations for all particles and active particles in Fig. 4.3. We find the linear relationship always works for the continuous particle size distribution. In this case, we assume that the granular material is a continuous particle size distributed soil. We extend the single grain contact series to a domain with minimum and maximum grain size  $S_{m,g}$  and  $S_{M,g}$ . We also employ the probability density function to characterize the effective contact stress for a specific size of grain-to-grain contact. Consequently, a cross-scale dissolution



FIGURE 4.3: Linear relationship of particle contact force between the particle passing by volume and contribution to the stress.

rate formulation is given as:

$$\dot{\xi}(s) = \int_{s_{m,g}}^{s_{M,g}} \frac{dM_{diss}}{M_0 dt} \tilde{g}(s) = \int_{s_{m,g}}^{s_{M,g}} \frac{3\pi V_m^2 k_+ \rho_g d_c^2}{4RT(\frac{1}{6}\pi s^3)} \sigma_{eff} \tilde{g}(s) ds \tag{4.33}$$

# 4.3 Numerical approach

### 4.3.1 Numerical implementation

This section introduces the numerical implementation of the constitutive model theory proposed in Section 4.2. We present the corresponding rate-dependent equations for the constitutive model and further give the classical returning mapping algorithm with a fully implicit approach.

We first list the relevant rate-dependent equations used for the plasticity model for sand under infinitesimal deformation conditions. TABLE 4.1: Algorithm 4-1: Summary of the rate-dependent equations used for the plasticity model

Algorithm 4-1: Summary of the rate-dependent equations used for the plasticity model

1. St	rain rates:	$\dot{oldsymbol{\epsilon}}=\dot{oldsymbol{\epsilon}}^e+\dot{oldsymbol{\epsilon}}^p$
2. Hy	yperelastic rate equations:	$\dot{oldsymbol{\sigma}}=oldsymbol{c}^e:\dot{oldsymbol{\epsilon}}^e;$
		$oldsymbol{c}^e = rac{\partial^2 \Psi_r}{\partial oldsymbol{\epsilon}^e \partial oldsymbol{\epsilon}^e}$
3. Fl	ow rule:	$\dot{oldsymbol{\epsilon}}^{p}=\dot{\lambda}rac{\partial\mathcal{F}}{\partialoldsymbol{\sigma}}$
4. De	egradation variables:	$\dot{\phi} = f(\dot{\xi});  \dot{\xi} = rac{dM_{diss}}{dtM_0},$
		see from Eqs. $(4.10)$ , $(4.13)$ , and $(4.32)$
5. Ha	ardening law:	$\dot{p}_c = f(\dot{\epsilon}_v); \dot{p}_b = f(\dot{\epsilon}_v, \dot{\epsilon}_s),$
		see from Eqs. $(4.28)$ , $(4.30)$
6. Co	onsistency condition:	$\Delta \dot{\lambda} \cdot \mathcal{F}(p,q,p_d,p_\alpha) = 0$
7. Ku	uhn-Tucker conditions:	$\dot{\lambda} \ge 0; \mathcal{F} \le 0$

In this case, we combine the aforementioned hyperelasticity with the plastic behavior and integrate the flow rule at time  $t_{n+1}$  in the space defined by the elastic strain. The return mapping algorithm for the space of a two-invariant Cam-Clay type model is employed, where:

$$\boldsymbol{\epsilon}_{n+1}^{e} = \boldsymbol{\epsilon}_{n+1}^{e \ tr} - \Delta \lambda_{n+1} \frac{\partial \mathcal{F}}{\partial \boldsymbol{\sigma}}|_{n+1}$$
(4.34)

with the volumetric and deviatoric components as follows:

$$\epsilon_{v\ n+1}^{e} = \epsilon_{v\ n+1}^{e\ tr} - \Delta\lambda_{n+1} \frac{\partial\mathcal{F}}{\partial p}|_{n+1}; \tag{4.35}$$

$$\epsilon_{s\ n+1}^{e} = \epsilon_{s\ n+1}^{e\ tr} - \Delta\lambda_{n+1}\frac{\partial\mathcal{F}}{\partial q}|_{n+1};$$
(4.36)

Following the Kuhn-Tucker conditions, in the elastic regime, the yield function should be  $\mathcal{F}(p,q,p_c,p_b) < 0$ . In other words, the trivial results  $\epsilon_v^e = \epsilon_v^e t^r$ ,  $\epsilon_s^e = \epsilon_s^e t^r$ ,  $p_c = p_{c,n}$ , and  $p_b = p_{b,n}$  should hold in the elastic region. The elastoplastic response should be solved in an iterative approach. The dependence of the gradients for  $\frac{\partial \mathcal{F}}{\partial p}$  and  $\frac{\partial \mathcal{F}}{\partial q}$  on the natural strain invariants follows,

$$\frac{\partial \mathcal{F}}{\partial p} = 2p - 2p_b - p_d - 2\frac{q^2}{\tilde{M}^3}\frac{\partial \tilde{M}}{\partial p}; \qquad (4.37)$$

$$\frac{\partial \mathcal{F}}{\partial q} = \frac{2q}{\tilde{M}^2} \tag{4.38}$$

The update for the internal variables  $p_c$  and  $p_b$  on the strain invariant follows the rate-dependent Eqs. (4.28), (4.30), which reads,

$$p_c = p_{c,n} e^{\frac{-(\epsilon_v^p - \epsilon_{v,n}^p)}{\hat{\lambda} - \hat{k}}} = p_{c,n} e^{\frac{-(\epsilon_v^{e,tr} - \epsilon_{v,n}^e)}{\hat{\lambda} - \hat{k}}}$$
(4.39)

and,

$$p_b = (1 - \phi_n) p_{b0} e^{-u \sqrt{\frac{2(\epsilon_v^p - \epsilon_{v,n}^p)^2 - 9(\epsilon_s^p - \epsilon_{s,n}^p)^2}{6}}} = (1 - \phi_n) p_{b0} e^{-u \sqrt{\frac{2(\epsilon_v^{e,tr} - \epsilon_{v,n}^e)^2 - 9(\epsilon_s^{e,tr} - \epsilon_{s,n}^e)^2}{6}}}$$
(4.40)

We employ the additive decomposition of natural strain invariants for volumetric and deviatoric, respectively. That are  $\epsilon_v = \epsilon_v^e + \epsilon_v^p = \epsilon_v^e t^r + \epsilon_{v,n}^p$  and  $\epsilon_s = \epsilon_s^e + \epsilon_s^p = \epsilon_s^e t^r + \epsilon_{s,n}^p$ . Therefore, the derivations from Eq. (4.34~4.40) contain the approach to solve the elastoplastic problem. This process can be treated as a system of simultaneous nonlinear equations in terms of the elastic strain invariants (since the relationships are all related to elastic parameters) and plastic multiplier  $\Delta \lambda$ .

Next, we introduce the solving method and derive the relevant components of locally iterative Newton's method below. We select the primary unknowns are  $\epsilon_v^e$ ,  $\epsilon_s^e$ , and  $\Delta\lambda$ . Consequently, we have the residual and Jacobian components used for iterations.

$$\begin{bmatrix} \mathbf{A} \end{bmatrix} \begin{bmatrix} \epsilon_v^e \\ \epsilon_s^e \\ \Delta \lambda \end{bmatrix} = \begin{bmatrix} \epsilon_v^e - \epsilon_v^e \ tr + \Delta \lambda \partial_p \mathcal{F} \\ \epsilon_s^e - \epsilon_s^e \ tr + \Delta \lambda \partial_q \mathcal{F} \\ \mathcal{F} \end{bmatrix}, \qquad (4.41)$$

where  $[\mathbf{A}]$  is a 3 × 3 Jacobian matrix, with its components detailed in Appendix A.7.

To clarify the derivations and notations of the components of the matrix  $[\mathbf{A}]$ , we proceed as follows. For example, for the chain rule of the derivation  $\frac{\partial_p \mathcal{F}}{\partial \epsilon_v^e} = \frac{\partial_p \mathcal{F}}{\partial p} \frac{\partial p}{\partial \epsilon_v^e} + \frac{\partial_p \mathcal{F}}{\partial q} \frac{\partial q}{\partial \epsilon_v^e}$ , we define  $\mathbf{D}^e = \nabla \nabla \phi$  (see definition in Eq. (4.27)) and  $\mathbf{H} = \nabla \nabla \mathcal{F}|_{p_c, p_b}$ . Consequently, the components of the matrices are:

$$\begin{bmatrix} \mathbf{D}^{e} \end{bmatrix} = \begin{bmatrix} D_{11}^{e} & D_{12}^{e} \\ D_{21}^{e} & D_{22}^{e} \end{bmatrix} = \begin{bmatrix} \partial_{\epsilon_{v}^{e} \epsilon_{v}^{e}}^{e} \Psi & \partial_{\epsilon_{v}^{e} \epsilon_{s}^{e}}^{e} \Psi \\ \partial_{\epsilon_{s}^{e} \epsilon_{v}^{e}}^{e} \Psi & \partial_{\epsilon_{s}^{e} \epsilon_{s}^{e}}^{e} \Psi \end{bmatrix},$$
(4.42)

$$\begin{bmatrix} \mathbf{H} \end{bmatrix} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} = \begin{bmatrix} \partial_{pp}^2 \mathcal{F} & \partial_{pq}^2 \mathcal{F} \\ \partial_{qp}^2 \mathcal{F} & \partial_{qq}^2 \mathcal{F} \end{bmatrix}.$$
 (4.43)

As we have shown in the aforementioned example for the chain rule, the multiplicative relation for the components of the Hessian matrix is,

$$\begin{bmatrix} \mathbf{G} \end{bmatrix} = \begin{bmatrix} \mathbf{H} \end{bmatrix} \begin{bmatrix} \mathbf{D}^e \end{bmatrix} = \begin{bmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{bmatrix} = \begin{bmatrix} H_{11}D_{11}^e + H_{12}D_{21}^e & H_{11}D_{12}^e + H_{12}D_{22}^e \\ H_{21}D_{11}^e + H_{22}D_{21}^e & H_{21}D_{12}^e + H_{22}D_{22}^e \end{bmatrix}$$
(4.44)

We simplify the expressions of matrix  $[\mathbf{A}]$  with the components of matrix  $[\mathbf{G}]$  in this case. The detailed formulations for all components of the matrices are given in Appendix A.6 and A.7. In the following algorithm, we present the return mapping algorithm which is performed in the strain invariant space.

TABLE 4.2: Algorithm 4-2: Summary of the return mapping algorithm for the plasticity model

Algorithm 4-2: Summary of the return mapping algorithm for the plasticity model

- **Step 1**. Elastic strain predictor:  $\epsilon^{e,tr} = \epsilon_n^e + \Delta \epsilon$
- **Step 2**. Calculate strain invariant:  $\epsilon_v^e, \epsilon_s^e$
- **Step 3.** Elastic stress predictor:  $\boldsymbol{\sigma}^{e,tr} = \frac{\partial \Psi^e}{\partial \boldsymbol{\epsilon}^e}$  with the updated  $p, q, p_{c,n}, p_{b,n}, \xi$ , and  $\phi$
- Step 4. Check if the material is yielding: if  $\mathcal{F} < \text{TOL}$ ? (with tolerance  $TOL = 1.0 \times 10^{-9}$ )
  - (i) YES:  $\boldsymbol{\epsilon}^e = \boldsymbol{\epsilon}^{e,tr}, \, \boldsymbol{\sigma}^e = \boldsymbol{\sigma}^{e,tr}, \, p_c = p_{c,n}, \, \text{and} \, p_b = p_{b,n}$
  - (ii) Calculate the fourth-order tangential elasticity tensor  $\mathbb{C}^e$  and return to Step 1
- **Step 5.** Plastic corrector:  $\epsilon^e = \epsilon^{e,tr} \Delta \lambda \cdot \frac{\partial \mathcal{F}}{\partial \boldsymbol{\sigma}}, \ \boldsymbol{\sigma} = \frac{\partial \Psi^e}{\partial \boldsymbol{\epsilon}^e}$
- **Step 6**. Update plastic internal variables:
  - (i) Calculate the updated strain invariant:  $\epsilon_v^e, \epsilon_s^e$
  - (ii) Update the chemical degradation relevant state parameters:  $\xi$ , and  $\phi$
  - (iii) Update the degraded stiffness:  $p = (1 \phi)^{\frac{2}{3}} p_n, q = (1 \phi)^{\frac{2}{3}} q_n$
  - (iv) Update the degraded bonding pressure:  $p_b = (1 \phi)p_{b,n}$
  - (v) Update preconsolidation pressure:  $p_c = p_{c,n}$
- **Step 7**. Assemble the Jacobian Matrix [A]

# **Step 8.** Newton-Raphson iteration for the step k to find if $\epsilon_v^e - (\epsilon_v^e)_k < \text{TOL}, \epsilon_s^e - (\epsilon_s^e)_k < \text{TOL}$ , and $\Delta \lambda - (\Delta \lambda)_k < \text{TOL}$ ? (with tolerance $TOL = 1.0 \times 10^{-9}$ )

(i) YES:  $\boldsymbol{\epsilon}^{e} = \boldsymbol{\epsilon}^{e,n} - \Delta \lambda \cdot \frac{\partial \mathcal{F}}{\partial \boldsymbol{\sigma}}, \ \boldsymbol{\epsilon}^{p} = \boldsymbol{\epsilon}^{p,n} + \Delta \lambda \cdot \frac{\partial \mathcal{F}}{\partial \boldsymbol{\sigma}}, \ \boldsymbol{\epsilon} = \boldsymbol{\epsilon}^{e} + \boldsymbol{\epsilon}^{p}, \ \lambda = \lambda_{n} + \Delta \lambda, \text{ and reconstruct } \mathbb{C}^{ep}$ 

TABLE 4.2: Algorithm 4-2: Summary of the return mapping algorithm for the plasticity model (continued)

Algorithm 4-2: Summary of the return mapping algorithm for the plasticity model (ii) NO: Go to Step 5 and recalculate Steps 5 to 8 with the updated  $(\Delta \lambda)_k$ 

#### 4.3.2 Algorithmic tangent operator

The algorithmic tangent operator can be expressed as  $\mathbb{C} = \frac{\partial \sigma}{\partial \epsilon^{e,tr}}$ , which is used for the global Newton iteration for FE problems. In this study, we provide the algorithmic tangent operator for both elastic and elastoplastic regions. The chemical degradation also occurs for both the elastic and plastic deformation regions. However, the hardening law captures the chemo-mechanical effects only within the plastic region.

To derive the elastoplastic algorithmic tangent operator, we first consider it for the elastic region. Referring to Eq. (4.24), the Cauchy stress tensor is expressed as,

$$\boldsymbol{\sigma} = p\mathbf{1} + \sqrt{\frac{2}{3}}q\hat{\boldsymbol{n}} \tag{4.45}$$

where we assume  $\hat{\boldsymbol{n}} = \frac{\boldsymbol{\gamma}^{e}}{\|\boldsymbol{\gamma}^{e}\|} = \frac{\boldsymbol{\gamma}^{e,tr}}{\|\boldsymbol{\gamma}^{e,tr}\|}$  is from the coaxiality of the principal directions. Then, according to the chain rule we have (Borja and Tamagnini, 1998; Borja, 2013),

$$\mathbb{C}^{e} = \mathbf{1} \otimes (D_{11}^{e} \frac{\partial \epsilon_{v}^{e}}{\partial \epsilon} + D_{12}^{e} \frac{\partial \epsilon_{s}^{e}}{\partial \epsilon}) + \sqrt{\frac{2}{3}} \hat{\mathbf{n}} \otimes (D_{21}^{e} \frac{\partial \epsilon_{v}^{e}}{\partial \epsilon} + D_{22}^{e} \frac{\partial \epsilon_{s}^{e}}{\partial \epsilon}) + \frac{2q}{3\epsilon_{s}^{e,tr}} (\mathbf{I} - \frac{1}{3} \mathbf{1} \otimes \mathbf{1} - \hat{\mathbf{n}} \otimes \hat{\mathbf{n}})$$
$$= (D_{11}^{e} - \frac{2q}{9\epsilon_{s}^{e,tr}}) \mathbf{1} \otimes \mathbf{1} + (\frac{2}{3} D_{22}^{e} - \frac{2q}{3\epsilon_{s}^{e,tr}}) \hat{\mathbf{n}} \otimes \hat{\mathbf{n}} + \frac{2q}{3\epsilon_{s}^{e,tr}} \mathbf{I} + \sqrt{\frac{2}{3}} (D_{12}^{e} \mathbf{1} \otimes \hat{\mathbf{n}} + D_{21}^{e} \hat{\mathbf{n}} \otimes \mathbf{1})$$
$$\tag{4.46}$$

where **1** is the second-rank identity tensor with components  $\delta_{ij}$  (the Kronecker delta).  $\mathbf{I}$  denotes rank-four symmetric identity operator with the components  $I_{ijkl} = \frac{\delta_{ik}\delta_{jl} + \delta_{il}\delta_{kj}}{2}$ . The symbol  $\otimes$  is used to form a dyad, also known as the outer product. For example,  $(\mathbf{a} \otimes \mathbf{b})_{ijkl} = a_{ij}b_{kl}$  for any second-order symmetric tensor  $\mathbf{a}$  and  $\mathbf{b}$ . The detailed expression of all terms for the algorithmic tangent operator  $\mathbb{C}^e$  is provided in Appendix A.5.

In the following context, we further introduce the derivation of the algorithmic tangent operator  $\mathbb{C}^{ep}$ , which means that the global integration considers both elastic and plastic regions. We follow the approach proposed by Borja and Andrade (2006). However, the final algorithmic tangent operator is tailored to the problem of this study. Firstly, we redefine the local residual in Eq. (4.41) with unknowns as,  $\mathbf{r} = \mathbf{r}(\epsilon_v^{e,tr}, \epsilon_s^{e,tr}, \mathbf{x})$ , where  $\mathbf{x}$  is the unknown vector as  $\boldsymbol{x} = \boldsymbol{x}(\epsilon_v^e, \epsilon_s^e, \Delta \lambda)$ . Globally, the strain derivation of the residual vector is:

$$\frac{\partial \boldsymbol{r}}{\partial \boldsymbol{\epsilon}} = \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{\epsilon}} |_{\boldsymbol{x}} + \left(\frac{\partial \boldsymbol{r}}{\partial \boldsymbol{x}}|_{\boldsymbol{\epsilon}_{v}^{e,tr},\boldsymbol{\epsilon}_{s}^{e,tr}}\right) \cdot \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{\epsilon}}$$
(4.47)

If we denote  $\mathcal{A} = \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{x}}|_{\epsilon_v^{e,tr},\epsilon_s^{e,tr}}$ , Eq. (4.47) is rearranged as:

$$\mathcal{A} \cdot \frac{\partial x}{\partial \epsilon} = -\frac{\partial r}{\partial \epsilon} \tag{4.48}$$

This means we can then express the derivation of the unknown vector as the inverse of matrix  $\mathcal{A}$  and denote it as  $\mathcal{B}$ , which reads:

$$\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{\epsilon}} = -\frac{1}{\mathcal{A}} \cdot \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{\epsilon}} = -\mathcal{B} \cdot \frac{\partial \boldsymbol{r}}{\partial \boldsymbol{\epsilon}}$$
(4.49)

We expand the Eq. (4.49) to vector and matrix as:

$$\begin{bmatrix} \frac{\partial \epsilon_v^{\varepsilon}}{\partial \epsilon} \\ \frac{\partial \epsilon_s^{\varepsilon}}{\partial \epsilon} \\ \frac{\partial \Delta \lambda}{\partial \epsilon} \end{bmatrix} = \begin{bmatrix} \mathcal{B}_{11} & \mathcal{B}_{12} & \mathcal{B}_{13} \\ \mathcal{B}_{21} & \mathcal{B}_{22} & \mathcal{B}_{23} \\ \mathcal{B}_{31} & \mathcal{B}_{32} & \mathcal{B}_{33} \end{bmatrix} \begin{bmatrix} -\frac{\partial \boldsymbol{r}_1}{\partial \epsilon} \\ -\frac{\partial \boldsymbol{r}_2}{\partial \epsilon} \\ -\frac{\partial \boldsymbol{r}_3}{\partial \epsilon} \end{bmatrix}, \quad (4.50)$$

The derivations for components of the vector  $\left[-\frac{\partial \boldsymbol{r}}{\partial \boldsymbol{\epsilon}}\right]$  are follows,

$$\begin{cases} -\frac{\partial \boldsymbol{r}_{1}}{\partial \boldsymbol{\epsilon}} = -\frac{\partial \boldsymbol{r}_{1}}{\partial \boldsymbol{\epsilon}_{v}^{e,tr}} \frac{\partial \boldsymbol{\epsilon}_{v}^{e,tr}}{\partial \boldsymbol{\epsilon}} = (1 - \Delta \lambda T_{1}) \mathbf{1} \\ -\frac{\partial \boldsymbol{r}_{2}}{\partial \boldsymbol{\epsilon}} = -\frac{\partial \boldsymbol{r}_{2}}{\partial \boldsymbol{\epsilon}_{s}^{e,tr}} \frac{\partial \boldsymbol{\epsilon}_{s}^{e,tr}}{\partial \boldsymbol{\epsilon}} = (1 - \Delta \lambda T_{2}) \sqrt{\frac{2}{3}} \hat{\boldsymbol{n}} \\ -\frac{\partial \boldsymbol{r}_{3}}{\partial \boldsymbol{\epsilon}} = -(\frac{\partial \boldsymbol{r}_{3}}{\partial \boldsymbol{\epsilon}_{v}^{e,tr}} \frac{\partial \boldsymbol{\epsilon}_{s}^{e,tr}}{\partial \boldsymbol{\epsilon}} + \frac{\partial \boldsymbol{r}_{3}}{\partial \boldsymbol{\epsilon}_{s}^{e,tr}} \frac{\partial \boldsymbol{\epsilon}_{s}^{e,tr}}{\partial \boldsymbol{\epsilon}}) = -T_{3} \mathbf{1} - T_{4} \sqrt{\frac{2}{3}} \hat{\boldsymbol{n}} \end{cases}$$
(4.51)

where the temporary derivations in Eq. (4.51) are defined as:

$$\begin{cases} T_1 = \frac{\partial_p \mathcal{F}}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_v^{e,tr}} + \frac{\partial_p \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_v^{e,tr}} \\ T_2 = \frac{\partial_q \mathcal{F}}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_s^{e,tr}} + \frac{\partial_q \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_s^{e,tr}} \\ T_3 = \frac{\partial \mathcal{F}}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_v^{e,tr}} + \frac{\partial \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_v^{e,tr}} \\ T_4 = \frac{\partial \mathcal{F}}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_s^{e,tr}} + \frac{\partial \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_s^{e,tr}} \end{cases}$$
(4.52)

We then derive the expressions for components of the unknown vector  $\left[\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{\epsilon}}\right]$  as:

$$\frac{\partial \epsilon_v^e}{\partial \epsilon} = -\mathcal{B}_{11} \frac{\partial \mathbf{r}_1}{\partial \epsilon} - \mathcal{B}_{12} \frac{\partial \mathbf{r}_2}{\partial \epsilon} - \mathcal{B}_{13} \frac{\partial \mathbf{r}_3}{\partial \epsilon} = \tilde{\mathcal{B}}_{11} \mathbf{1} + \tilde{\mathcal{B}}_{12} \sqrt{\frac{2}{3}} \hat{\boldsymbol{n}}$$
(4.53)

$$\frac{\partial \epsilon_v^e}{\partial \epsilon} = -\mathcal{B}_{21} \frac{\partial \mathbf{r}_1}{\partial \epsilon} - \mathcal{B}_{22} \frac{\partial \mathbf{r}_2}{\partial \epsilon} - \mathcal{B}_{23} \frac{\partial \mathbf{r}_3}{\partial \epsilon} = \tilde{\mathcal{B}}_{21} \mathbf{1} + \tilde{\mathcal{B}}_{22} \sqrt{\frac{2}{3}} \hat{\boldsymbol{n}}$$
(4.54)

where the definitions in Eq. (4.51), (4.52) are substituted in Eq. (4.53) (4.54). We list the rearrangement of the definitions as:

In this case, we introduce Eq. (4.53), (4.54) into Eq. (4.46). The algorithmic tangent operator  $\mathbb{C}^{ep}$  is,

$$\mathbb{C}^{ep} = (D_{11}^{e}\tilde{\mathcal{B}}_{11} + D_{12}^{e}\tilde{\mathcal{B}}_{21} - \frac{2q}{9\epsilon_{s}^{e,tr}})\mathbf{1} \otimes \mathbf{1} + \sqrt{\frac{2}{3}}(D_{11}^{e}\tilde{\mathcal{B}}_{12} + D_{12}^{e}\tilde{\mathcal{B}}_{22})\mathbf{1} \otimes \hat{\mathbf{n}} \\
+ \sqrt{\frac{2}{3}}(D_{21}^{e}\tilde{\mathcal{B}}_{11} + D_{22}^{e}\tilde{\mathcal{B}}_{21})\hat{\mathbf{n}} \otimes \mathbf{1} + \frac{2}{3}(D_{21}^{e}\tilde{\mathcal{B}}_{12} + D_{22}^{e}\tilde{\mathcal{B}}_{22})\hat{\mathbf{n}} \otimes \hat{\mathbf{n}} + \frac{2q}{3\epsilon_{s}^{e,tr}}(\mathbf{I} - \hat{\mathbf{n}} \otimes \hat{\mathbf{n}}) \\
= (\bar{D}_{11} - \frac{2q}{9\epsilon_{s}^{e,tr}})\mathbf{1} \otimes \mathbf{1} + \sqrt{\frac{2}{3}}(\bar{D}_{12}\mathbf{1} \otimes \hat{\mathbf{n}} + \bar{D}_{21}\hat{\mathbf{n}} \otimes \mathbf{1}) + \frac{2}{3}\bar{D}_{22}\hat{\mathbf{n}} \otimes \hat{\mathbf{n}} + \frac{2q}{3\epsilon_{s}^{e,tr}}(\mathbf{I} - \hat{\mathbf{n}} \otimes \hat{\mathbf{n}}) \\$$
(4.56)

where we define a new matrix  $[\bar{D}]$  as,

$$\begin{bmatrix} \bar{\boldsymbol{D}} \end{bmatrix} = \begin{bmatrix} \bar{D}_{11} & \bar{D}_{12} \\ \bar{D}_{21} & \bar{D}_{22} \end{bmatrix} = \begin{bmatrix} D_{11}^e & D_{12}^e \\ D_{21}^e & D_{22}^e \end{bmatrix} \begin{bmatrix} \tilde{\mathcal{B}}_{11} & \tilde{\mathcal{B}}_{12} \\ \tilde{\mathcal{B}}_{21} & \tilde{\mathcal{B}}_{22} \end{bmatrix}$$
(4.57)

## 4.4 Evaluation the model response

In this section, we evaluate the proposed model from different viewpoints. We first validate the model by considering the bonding and stiffness degradation effects respectively. The comparisons help us confirm the capability of the model to capture only one of the impacts of the chemo-mechanical coupled performance, which is the reduced result from the proposed model. We then present the specific influences on the macro-stress-strain performance and especially on the plastic performance. Finally, we search for similar laboratory experiments and compare them against our model to evaluate the overall performance.

#### 4.4.1 Model validation

#### 4.4.1.1 Model calibration procedure

We need to first calibrate the material parameters for the proposed model. In fact, we can follow the standard calibration procedures to determine the parameters for the different materials. We introduce the general way for our model to obtain the parameters by using the macro- and micro-experimental data presented by Lagioia and Nova (1995); Ciantia et al. (2015a,b); Viswanath and Das (2020) for carbonate rock/soil (such as calcarenites). The model presented in this paper includes 18 parameters:

- Yield surface initial size:  $p_{c0}$ ,  $p_{b0}$ ,  $p_{u0}$ ,  $p_{d0}$ ;
- Yield surface shape:  $M, \tilde{\alpha}$ ;
- Mechanical hardening-softening:  $\hat{\lambda}, u;$
- Chemical hardening-softening:  $\alpha$ ,  $\beta_1$ ,  $\beta_2$ ,  $\kappa$ ,  $v^{solid}$ ,  $\beta$ , m,  $s_{M0}$ ,  $s_{m0}$ ;
- Elastic parameters:  $G_0$ ,  $\tilde{k}$ , b.

The yield surface initial size decides the initial elastic region of the material. Parameters  $p_{c0}$  and  $p_{b0}$  can be approximated by compression/tension tests (such as an isotropic compression test and an unconfined compression drained test). For example, Airey (1993) conducted the measurement for the tensile strengths using the indirect Brazillian split cylinder test.  $p_{u0}$  and  $p_{d0}$  are calculated by the definition of the back stress and the revised preconsolidation pressure of the reconstituted soil corresponding to the cementation of the soil, respectively. M is the critical state stress ratio of the original MCC model.  $\tilde{\alpha}$  reflects the combination of the volumetric hardening of the MCC model and the shearing of the linear friction model, with this parameter representing their properties, which can be decided by the conventional triaxial test. The mechanical hardening-softening parameters  $\hat{\lambda}$ , u for the revised preconsolidation pressure can be obtained by an oedometer test. The chemical hardening-softening parameters are mostly decided by chemical reaction tests.  $\alpha$ ,  $\beta_1$ ,  $\beta_2$ ,  $\kappa$ , and  $v^{solid}$  are decided by the mineral categories. m is the fractal dimension that is considered to be independent of dissolution. It is a function of the particle size distribution, particle morphology, and pore structure. For the different material properties, some relationships can be employed to determine this value (Li et al., 2022).  $s_{M0}$  and  $s_{m0}$  are particle sizes that can be determined by the sieving method and X-ray images (Rodriguez et al., 2013).  $G_0$ ,  $\tilde{k}$  are traditional parameters appearing in the MCC model can be calibrated based on conventional triaxial tests on remolded specimens. b represents the interparticle bonding for  $p_u$  and  $p_b$ , which is assumed to be linear as the initial ratio of  $\left(\frac{p_{b0}}{p_{u0}}\right)$  (Yu et al., 2007).

#### 4.4.1.2 Model validation for the structured soil with bond

There are some test reports of natural clays that we can refer to in the literature. We select the representative test data on an intact stiff clay (Pietrafitta clay) that was reported by Burland et al. (1996). Figure 4.4 shows the comparison result for the one-dimensional consolidation. The key parameters for the model include Poisson's ratio v is 0.2; compressibility index is  $\hat{\lambda} = 0.227$ ,  $\tilde{k} = 0.051$ , respectively; critical state stress ratio M = 1.13, and the weighted parameter  $\tilde{\alpha} = 0.8$ . Moreover, we consider the mechanical degradation of the bonds but do not consider chemical degradation in this case. Therefore,  $\phi = 0.0$  and u = 0.16. In addition, we consider the coupled elastic modulus in our model. We then set the coupling parameter t = 1.0. Good agreement of the consolidated soil



FIGURE 4.4: Comparison results for the Pietrafitta clay between experimental data and numerical model.

between experimental and simulated results can be readily observed in Figure 4.4. We set the initial bonding pressure the same as in the experiment 1300 kPa. Compared with
the performance of the unbonded soil (illustrated by the dashed line), the improvement of the soil can be easily checked in the diagram. The bond is degraded due to the load transfer between the contacted bonds, which is determined by the material parameter (damage rate u).

#### 4.4.1.3 Model validation for the stiffness degradation with dissolution

Viswanath and Das (2020) performed oedometer tests to study the effect of dissolution on the elastic stiffness. They conducted compaction on two different relative densities (uniform grain size distribution at void ratios  $e_{max} = 0.82$ ,  $e_{max} = 0.72$ ) for the chemically degraded calcite granules. Figure 4.5 and Figure 4.6 present the oedometric response of the degraded calcite granules at different initial degrees of dissolution. The comparisons are carried out for selected degrees of dissolution as 0%, 12%, 23%, 31%. As described in their experimental test, the confining pressure of 10 kPa is initially applied, and the vertical stress is increased to 580 kPa in increments of 116 kPa.



FIGURE 4.5: Dense calcite granules' response for different degrees of dissolution.

In our model, we control the strain increment to realize the deviatoric load to the stress-point test. As we presented in Figures 4.5, 4.6, two cycles of loading and unloading are performed both for each experimental and numerical test. The relationships between e-p' depicted in the figures are almost identical between experimental data and simulation



FIGURE 4.6: Loose calcite granules' response for different degrees of dissolution.

results. We find that no matter whether it is dense or loose, the compressibility of the degraded sample is lower than the original ones.

### 4.4.2 Parametric study

#### 4.4.2.1 Effects of chemical processes on the stress-strain response

Figures 4.7 and 4.8 illustrate the predicted stress-strain response at varying initial bonding pressures and varying times for chemical reactions before applying the loading. For those two scenarios, we consider the compression and tension loading for the sample. Figure 4.7 presents the capability of the model to capture both mechanical and chemical degradation during loading processes. We also depict the simultaneous dissolution of cement bonds for the specific initial bonding pressure  $p_u = 350$  kPa case. With the increasing initial bonding pressure, the elastic response for compression and tension expands accordingly. We can see a similar trend for the stress-hardening and stress-softening responses for the different cement bonding values. This prediction is reasonable and is a direct outcome of the increment of the cement bonds, which we have validated in Section 4.4.1. We now introduce  $K_0$  compression with the confining pressure path as 50 kPa. The chemomechanical degradation occurs at the initial condition for bonding pressure  $p_u = 350$  kPa. As we see from the simultaneous chemical degradation after the time 6 h, 12 h, 24 h, and



FIGURE 4.7: Effect of bond dissolution on the strain-stress response both for undrained compression test and tension test.

48 h, the stress-softening effects become much more obvious. The chemical force during chemo-mechanical degradation remains the same  $\frac{Q}{K_{eq}} = 0.5$  for all cases. The reaction constant for the bond is configured to be  $\kappa = 8.64e^{-8} \frac{mol}{mm^2 \cdot h}$ . From the first 6 h, we see a quick drop in the deviatoric stress. Over time, the chemical softening effect stabilizes, particularly between 24 to 48 hours.

We now turn our focus to look at the influence of grain stiffness degradation on the stress-strain response. We pick up the initial bonding pressure  $p_u = 350$  kPa case. The solid curves in Figure 4.8 illustrate the chemical-induced degradation on bonds, while dash curves present the chemical-induced degradation on both grains and bonds. The reaction constant for a grain is  $\kappa = 9.52e^{-12} \frac{mol}{mm^2 \cdot h}$ . The chemical force driving the degradation is the same as for the cases shown in Fig. 4.7. It is clear here that the model captures the stiffness degradation due to the dissolution of grain. Compared with the pure bond degradation, the higher softening effect is presented over the continuous chemical reaction processes in this case. The cumulative strain shows higher accumulations both for elastic and inelastic strains. The stiffness degradation is not as fast as the bonding degradation since we set different reactions constant. This also results in the not-always softening effects for treating specimens at different times, such as between 24 h and 48 h within the strain range between 0.1 to 0.15 in Fig. 4.8. It is worth noting that



FIGURE 4.8: Effect of grain and bond dissolution on strain-stress response both for undrained compression test and tension test.

such forms of inelastic deformation mechanisms have been observed in the laboratory tests conducted on granular soils and cemented materials (Castellanza and Nova, 2004; Shin and Santamarina, 2009; Ciantia et al., 2015b). We now validate our model with laboratory experiments to evaluate the performance of the model to capture this kind of phenomenon.

# 4.4.2.2 Effects of chemical processes on the elastic stiffness and plastic internal variables

In this section, we carry out a parametric study for the internal variables to explore the evolution in the elastic stiffness and cemented bonding pressure due to the grain size and applied pressure during chemical degradation. Figure 4.9 denotes the results between grain size distribution and stiffness. We collect the stiffness evolution for different chemically induced grain sizes. The bulk modulus decreases with higher degradation in the size of the grains for a given mean stress. With higher mean effective stress applied to the sample, the overall stiffness can be enhanced due to the constraints on the displacement behavior. This result is reflected on the evolution of the Hessian matrix defined in Eq. (4.27). However, the tendency of the stiffness degradation is similar no matter if it is high or low mean effective stress is applied. That is partially because of the grain-to-grain and grain-to-bond simplification using the grain size distribution.

We now explore the plastic internal variables corresponding to the bond and grain test in Figures 4.7 and 4.8. As we can see from Figures 4.10 and 4.11, the internal variables remain constant during the hyperelasticity. However, the stiffness degradation is reflected to the yield values expanding or contracting as a functional of the internal variables.



FIGURE 4.9: Stiffness degradation due to different chemical degradation and mean effective stress.

With chemical degradation working on plasticity, the performance of the internal variables is completely different. Firstly, it is easy to imagine that the internal variable for a bond keeps reducing due to chemical degradation until it ultimately fails. This is captured in our model. When we further consider the degradation of grains and bonds, we find that the hyperelastic region affects changes in the stress-strain response in a manner similar to translation. At the same time, comparing the simulation results in Section 4.4.2.1, we can see that the softening effect caused by chemical degradation, in this case, is the main reason that directly leads to the sudden drop in material strength, rather than mechanical degradation.

#### 4.4.3 Model performance against laboratory experiments

Section 4.4.2 addresses the quantity of different factors of the model. It was shown that softening mechanisms on grain and bond dissolution were captured. However,



FIGURE 4.10: Internal variable evolution considering chemicallyinduced bonding degradation.



FIGURE 4.11: Internal variable evolution considering chemicallyinduced grain and bonding degradation.

the comprehensive performance of our model to capture the interactions between the evolution of the microscopic structure and the deformation response of the granular porous media due to chemo-mechanical forcing still needs to be validated with laboratory experiments for different types of loading conditions. In our validation examples, we simulate both the deterioration of the material and the strengthening of the material working cases in geotechnical engineering.

We first perform a series of unconfined compression tests at the different values of mass dissolution ratio  $\xi$ . The experimental data is taken from Ciantia et al. (2015b). We note that the laboratory experiments were carried out under controlled dissolution. They presented the strengthened degradation of calcarenite samples from Canosa, Italy. In our model, we adjust the reaction constants and the exposure time to the acid solution to achieve target experimental values for the dissolution rate. Overall, our model reproduces the softening tendency of the degraded calcarenite shown in Figure 4.12. We get similar peak stress states for the different dissolution cases. However, the discrepancies before and after the peak are obvious compared with experimental data. We test our model and compare it to the literature verifying the same cases (Gajo et al., 2015; Buscarnera and Das, 2016). We believe that two main reasons inducing the discrepancies. First, in our model, the degradation due to chemo-mechanical induced reasons is contained in a degradation evolution function. The mechanisms, including grain and bond crush, are not precisely included in the chemical processes. The reactive surface area increment due to crushing may have had a greater influence on the degradation. In addition, we clarify that the model in this study characterizes the degradation of grain and bond separately by using the degradation function  $\phi$  and considering different reaction rate contributions from grain and bond. However, the contributions are difficult to match with the experimental data since the original data is reported with the total mass dissolution (Buscarnera and Das, 2016). In fact, in our model, we simplify it as the same dissolution mass for the grains and bonds. In hyperelasticity, we only consider the degradation of stiffness, while in plasticity we consider both. The detailed simulation parameters are shown in Table 4.3 column for set No. 1.

We also check the internal variable evolution for the above dissolution cases. The preconsolidation pressure and cementation bonding pressure are both plotted in Figure 4.13. As discussed in the theoretical sections, the preconsolidation pressure remains constant in the elastic region but increases in the plastic region under the given stress state in this case. This phenomenon is captured here. It is also influenced by the mass dissolution rate. We observe that the hardening effects are sensitive to the initial



FIGURE 4.12: Effect of grain and bond dissolution on strain-stress response both for undrained compression test and tension test.

mass dissolution loss. The further process for hardening is mainly controlled by the volumetric strain evolution. However, the pressure for cementation is greatly influenced by the softening of the cemented bond. With the increasing strain of the sample, there is competition between preconsolidation and cementation pressure. When the consumption of cemented bonds exceeds a certain value, the plasticity then is mainly governed by preconsolidation. The phenomena are reflected at the end of the loading in the strain-stress diagram.

More loading conditions are now validated by referring to the experimental work done by Airey (1993). Their laboratory tests on cemented carbonate (calcarenite) soils from the North West Shelf of Australia were conducted using both conventional and various trial stress paths. The estimation of the degree of cementation was performed by a series of tensile tests. Airey (1993) emphasized the complication of the interpretation of the variations for the cementation and the sensitive impacts on the mechanical response. As we observed in Eq. (4.9) the dissolution and precipitation can be captured in our chemical thermodynamic equation. We validated several cases to test the dissolution impacts on bonds. However, the last example here is simulated with the precipitation for the bonds. We control the chemical reactions to precipitate to simulate the higher cementation of the bonds in the soil. The comparison of laboratory mechanical response is referred to the experiments corresponding to the tested cementation in simulations (Buscarnera and Das,



FIGURE 4.13: Internal variables response both for undrained compression test and tension test.

2016). We simulate for the drained and undrained test. The deviator stress  $q = (\sigma'_1 - \sigma'_3)$ and axial strain  $\epsilon_a$  responses from a series of drained and undrained tests are shown in Figure 4.14 and Figure 4.15. In these tests, the samples were isotropically consolidated to the mean effective stress. We keep the same confining pressure as those tests, which are listed in Table 4.3. For the drained tests, the deviator stresses increase linearly up to a well-defined yield point, followed by a further gradual rise towards an ultimate state accompanied by significant volumetric strains. However, we notice that as the bonds precipitate, the sample becomes denser than originally. Experimental data show that there is a softening phase at strains between 0.02 - 0.04, occurring for higher cementation. The simulation results make it difficult to capture that phenomenon. We believe that the main reason is that the coupled relations for chemo-mechanical in our model are weak. We simply multiply the macroscopic parameters by the degradation effects of chemical reactions, even though the multiplier originates from microscopic processes. This approach is verified for dissolution cases but is less effective for precipitation in cases of smaller porosity. Gajo et al. (2015, 2019) used an interpolation concept to approximate the degradation effects between maximum and minimum porosity of the sample, which is anticipated to be an improvement of our model in the future.

Finally, we compare the simulation results with the undrained triaxial test data presented in Figure 4.15. The experimental data are sourced from the work of Airey (1993). The experimental data show that all samples exhibit a stiff response up to a



FIGURE 4.14: Comparison of simulation results against the drained triaxial test responses from laboratory experimental tests.



FIGURE 4.15: Comparison of simulation results against the undrained triaxial test responses from laboratory experimental tests.

well-defined yield point, followed by an approximately linear relationship between deviator stress and axial strain. Note that the parameters used for the simulations shown in Figures 4.14 and 4.15 are provided in Table 4.3.

Parameter symbol	Description [Unit]	Set No. 1	Set No. 2
$G_0$	Initial shear modulus (MPa)	110	200
$\hat{\lambda}$	Slope of normal consolidation line	0.2	0.19
$ ilde{k}$	Slope of reload/unload line	0.05	0.006
$\alpha$	Chemical reaction weight factor	0.85	0.85
eta	Fractal dimension number	2.8	2.8
$\beta_1$	Material reaction parameter $(1/day)$	20000	20000
$\beta_2$	Material reaction parameter $(1/day)$	0.1	0.1
$\kappa$	Chemical reaction constant $(mol/(mm^2 day))$	9.52E-9	9.52 E- 9
$v^{solid}$	Molar volume of solid (g/mol)	143.93	143.93
m	Homothetic dissolution parameter	3	3
$s_{M0}$	Maximum size of grain/bond (mm)	2.0	2.0
$s_{m0}$	Minimum size of grain/bond (mm)	0.06	0.06
b	Ratio number of interparticle bond	0.089	0.089
u	Damage rate constant	0.3	0.3
M	Cam-Clay constant	1.35	1.84
$ ilde{lpha}$	Yield surface shape constant	0.6	0.8
$p_{b0}$	Initial bond cementation (kPa)	1200	500

TABLE 4.3: Simulation parameters used for validation against laboratory experiments.

### 4.5 Summary

In this paper, we presented a theory to model the evolution of the chemo-mechanical properties of cemented granular soil. The constitutive formulations were derived through the thermodynamics of chemical reactions occurring at the microstructural level. To upscale the microstructural effects to macroscopic continuum formulations, we employed cross-scale relations that connect the alterations of the soil skeleton and cement bonds. In the cross-scale relations, probability density functions were integrated into the contact forces between grain-to-grain and grain-to-bond interactions. This approach enables the chemo-mechanical model to capture both pore geochemistry and pressure

dissolution phenomena effectively. Additionally, we provided a detailed algorithmic tangent operator for solving finite element (FE) boundary value problems. The proposed model effectively captured stiffness degradation and debonding effects in geotechnical engineering. Simultaneously, the model preserved the concise properties of classical constitutive models while incorporating complex microscopic chemical processes. However, this work did not consider the impact of the geometry and contact laws of grains and bonds. Introducing a homogenization approach to account for the factors could enhance the predictive capability of the model.

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### Chapter 5

## Closure

### 5.1 Scope and contribution

In this dissertation, the author explored geological materials' theoretical and computational aspects for failure mechanisms associated with the coupled multiphysics processes. The comprehensive computational framework incorporated complex mechanical and chemical mechanisms across multiple scales via the finite element method and the newly developed constitutive models.

To realize the above general goals, the dissertation covered microscopic to macroscopic points of view that reflect the key physical processes according to the different application problems:

- The general calcite dissolution and precipitation processes in the pores of geological material, as well as their transport within the material during deformation, were considered.
- The components of sandstone for the multi-mineral system was considered via the mass balance of the corresponding minerals;
- Failure mechanisms of the geological material were addressed considering hydraulic fracturing and chemical degradation effects;
- Microscopic chemical reaction processes were combined with mechanical-chemical degradation from the constitutive level through to the internal variables (e.g. grains, bonds, chemical species, etc.).

These features were materialized through mathematical formulations, with the corresponding governing equations discretized and simulated using the finite element method.

In Chapter 2, we presented a computational framework to establish local chemical equilibrium at the macroscopic continuum scale to capture the coupled chemo-hydromechanical processes in saturated porous media using the finite element method. It was shown that the geochemistry of reactive multi-component systems can incorporate different sets of chemical reactions and characterize mineral reactions using the saturation index, which can then be linked to changes in porosity and permeability. This work provided a feasible approach to incorporate more complex geochemistry models into the poromechanics computational framework. The chapter addressed key theoretical and computational issues for capturing the displacements resulting from intra-aqueous chemical reactions occurring inside pores and the kinetic rate-limiting chemical reactions occurring on the surface of reactive minerals.

Subsequently, Chapter 3 described a computational framework utilizing the phase field approach to capture the coupled chemo-hydro-mechanical interactions within brittle porous media. The local chemical equilibrium system was extended to consider more complex acid-mineral reactions in sandstone. Changes in porosity and permeability were linked with the geochemistry models to ensure accurate mass exchanges and constitutive responses to flow and poroelasticity. Our main contribution was deriving chemical and mechanical degradation parameters within the phase field framework. The chemical degradation was connected with the changes in porosity, thereby influencing the mechanical behaviors of geomaterials via a comprehensive interplay of fluid transport and solid crack propagation.

Lastly, in Chapter 4, to account for the intrinsic anisotropy of geomaterials arising from their microstructure, such as grain and bond sizes, and reactivity, we provided a theory to model the evolution of the chemo-mechanical properties of cemented granular soil. The main contribution of this work was to introduce a way to upscale microstructural effects to the macroscopic continuum formulations. The cross-scale relations connected the alterations of the soil skeleton and cement bonds, considering both the pore geochemistry and pressure dissolution phenomena. It was shown that the fascinating aspect of this constitutive model is that the cross-scale relation can be integrated into classical constitutive models, providing an extension for considering the complex effects of chemical reactions on a material's mechanical behaviors.

Overall, this dissertation explores the development of an advanced modeling and simulation framework for a multiphysics system, incorporating the multiscale effects of chemical reactions on material properties. While this research provides a comprehensive computational framework for analyzing the mechanical response of geomaterials affected by chemical reactions during fluid transport, certain limitations must be acknowledged. One of the primary constraints arises from the limited understanding of the complex interaction mechanisms between chemical reactions and solid materials. The intricacies of these interactions are not fully captured by the current state of knowledge, which may affect the accuracy of the modeled behavior. Furthermore, the numerical methods employed, despite their robustness, are inherently limited in their ability to fully replicate real-world scenarios. Therefore, while the computational framework serves as a valuable predictive tool for engineering projects, the results should not be regarded as exact representations of reality. Instead, they provide informed estimations that must be complemented by experimental validation and field observations.

### 5.2 Future perspective

This study focused on the development, implementation, and application of a computational framework to investigate the safety and resilience of infrastructure systems undergoing complex multiphysics processes. A detailed explanation was provided to clarify the approaches proposed to reproduce and predict the coupled thermo-hydro-mechanical behavior of geomaterials. However, as the saying goes, Every step forward reveals new challenges. There are further topics and issues associated with these new challenges that require extended consideration and development.

One important consideration is that the transfer of information for certain parameters is not always a one-to-one mapping from microscopic parameters to macroscopic parameters. This issue is particularly evident in parameters that describe geochemical dynamics. There is a lack of consistent physical meanings and measurements to unify the variables at different scales and accurately reflect them in continuum-scale descriptions. On the contrary, the coupling of multiphysics processes already occurs at finer scales. For example, the dynamic reaction rate is significantly influenced by the effective reactive surface area. However, these coupling effects are not as simple as upscaling the quantities of those parameters. The mechanisms governing dynamic geochemistry to form mineralogical heterogeneity develop at finer scales. Therefore, the hybrid approach to consider subdomains and conservation, including mass and flow transport, should be examined using pore-scale equations. However, representing pore-scale models in a mechanistic manner is key to improving the predictive capability of coarser scale models, which remains a challenge.

For chemically induced crack propagation, we characterized the chemical degradation

parameter as an additional factor that contributes to the weakening of the damaged area in porous media, which is reflected macroscopically as changes in porosity. This is a straightforward way to consider the essence of chemical damage. However, regarding the chemical degradation of frictional contact with surface roughness, the consideration is closer to the essence of mechanical degradation induced by chemical reactions for geomaterials. Frictional contact is particularly important because it directly governs mechanical behavior at interfaces, where chemical degradation can accelerate wear, reduce shear strength, and lead to localized failure effects that cannot be fully explained by changes in porosity alone. By focusing on frictional contact with roughness, we aim to capture these intricate interactions between chemical processes and mechanical behaviors. This approach allows for a more accurate representation of how chemical reactions influence mechanical degradation, especially in complex systems like geomaterials. For a comprehensive description of such chemical degradation affecting mechanical behaviors, more sophisticated and fundamental functions are needed. This shift towards a more fundamental and detailed treatment of chemical degradation is essential for improving our understanding of the coupled processes and for developing models that can more reliably predict the long-term stability and performance of geomaterials under various environmental conditions.

Finally, my future research application areas may include:

- Modeling and analyzing multi-physics in rock/soil or granular porous media under complex environmental conditions: This is crucial for various applications, such as earth resources engineering, CO<sub>2</sub> sequestration engineering, offshore systems for energy production and resilient infrastructure, and assessing hazards caused by extreme weather, including the stability of slopes with weak interlayers due to acid rain.
- Modeling, designing, and optimizing chemically induced strengthening techniques: This is an ecological and effective treatment choice in modern geotechnical engineering. For example, the development of Microbial-Induced Calcite Precipitation (MICP) has progressed from basic scientific discoveries to advanced, practical applications in geotechnical engineering. Integrating MICP with advanced modeling techniques, such as finite element modeling (FEM) and discrete element modeling (DEM), allows for more accurate predictions of soil behavior and optimization of stabilization treatments. Multi-scale modeling provides insights into the interactions between bacterial activity, chemical reactions, and the mechanical properties of soils. This represents a future application for our computational framework.

# Appendix

### A.1 A Taylor-Galerkin scheme for convective transport

For the convective term in Eq. (2.34), we adopt a two-step Taylor-Galerkin algorithm. This method is based on a Taylor expansion in time of the solution at time step n. So, we have,

$$c_i^{n+\frac{1}{2}} = c_i^n + \frac{\Delta t}{2} (\frac{\partial c_i}{\partial t})^n, \tag{A.1}$$

$$(\frac{\partial c_i}{\partial t})^n = -\nabla \cdot \boldsymbol{F}_i^n,\tag{A.2}$$

where the concentration flux is defined as  $\boldsymbol{F}_i = (\tilde{\boldsymbol{v}}c_i)^n$ . consequently,

$$c_i^{n+\frac{1}{2}} = c_i^n + \frac{\Delta t}{2} (-\nabla \cdot F_i^n).$$
 (A.3)

Then, we can obtain flux at time  $n + \frac{1}{2}$  and use them in the second step:

$$c_i^{n+1} = c_i^n + \Delta t \left(\frac{\partial c_i}{\partial t}\right)^{n+\frac{1}{2}} = c_i^n - \Delta t \nabla \cdot \boldsymbol{F}_i^{n+\frac{1}{2}}.$$
 (A.4)

As for the  $\nabla F_i^{n+\frac{1}{2}}$ , we give the below derivations.

$$\frac{\partial \boldsymbol{F_i}^{n+\frac{1}{2}}}{\partial c_i} = \tilde{\boldsymbol{v}}^{n+\frac{1}{2}} \frac{\partial c_i^{n+\frac{1}{2}}}{\partial c_i} \tag{A.5}$$

$$\frac{\partial c_i^{n+\frac{1}{2}}}{\partial c_i} = \frac{dc_i^n}{dc_i} - \frac{\Delta t}{2} \nabla \cdot \frac{F_i^n}{\partial c_i}$$
(A.6)

$$\nabla \cdot \frac{\boldsymbol{F_i}^n}{\partial c_i} = \nabla \cdot (\tilde{\boldsymbol{v}})^n \tag{A.7}$$

$$\nabla \cdot (\tilde{\boldsymbol{v}})^n = \nabla \cdot (-\frac{\kappa}{\nu} \nabla p)^n \tag{A.8}$$

# A.2 The initial aqueous concentration for time-dependent dynamic reaction

This initial configuration of the chemical species concentration is used in Section 2.5 (verification example: chemical equilibrium with calcite dissolution and classical Terzaghi's two-dimensional consolidation).

component	Molality
$\mathrm{H}^+$	$9.787 \times 10^{-7}$
$\mathrm{Ca}^{2+}$	$3.723 \times 10^{-4}$
$\mathrm{HCO}_3^-$	$2.102\times10^{-4}$
$\mathrm{CO}_3^{2-}$	$1.128 \times 10^{-8}$
$OH^-$	$1.133\times10^{-8}$
$CaCO_3^{0}$	$5.131 \times 10^{-9}$
$\operatorname{CO}_2^{\ 0}$	$6.870\times10^{-4}$

TABLE A.1: Initial chemical species concentration for timedependent reaction

### A.3 Finite element discretization

The appendix section introduces the weak form of the governing field equations and provides the specific expressions for the semi-discretization in Eqs. (3.58) to (3.65). We first summarize the weak forms of the field equations along with the initial and boundary conditions. We also describe the standard weighted residual procedure used to derive the weak-form equations. Furthermore, the Galerkin form of the relevant matrices and vectors is illustrated. We then specifically clarify the two-step discretization procedure for the transport equation of chemical species.

### A.3.1 Weak form

We summarize the field governing equations with the primary unknown variables  $\boldsymbol{u}$ , p,  $\phi$ ,  $c_{\text{HF}}$ ,  $c_{\text{H}_2\text{SiF}_6}$ ,  $c_{\text{M}_1}$ ,  $c_{\text{M}_2}$ ,  $c_{\text{M}_3}$  as follows,

$$\nabla \cdot (\boldsymbol{\sigma}' - g(\phi, \phi^{chem}) p \boldsymbol{I}) + p \nabla \phi + \boldsymbol{f} = \boldsymbol{0}, \tag{A.9}$$

$$\partial_t (\rho \chi_R \nabla \cdot \boldsymbol{u}) + \nabla \cdot (-\rho \frac{\boldsymbol{K}}{\nu} \cdot (\nabla p + \rho \boldsymbol{g})) - q = 0, \qquad (A.10)$$

$$\frac{G_c}{l_0}(\phi - l_0^2 \nabla^2 \phi) = \mathcal{H},\tag{A.11}$$

$$\partial_{t}(H_{1}n + H_{2}w)c_{\rm HF} + \nabla \cdot ((H_{1}n + H_{2}w)vc_{\rm HF}) - \nabla \cdot ((H_{1}n + H_{2}w)D_{\rm HF} \cdot \nabla c_{\rm HF}) + \sum_{\rm mineral=1}^{3} (E_{i}c_{\rm Mi}(H_{1} \cdot S_{i}^{\star}(1-n) + H_{2})) = 0,$$
(A.12)

$$\partial_{t}(H_{1}n + H_{2}w)c_{H_{2}SiF_{6}} + \nabla \cdot ((H_{1}n + H_{2}w)vc_{H_{2}SiF_{6}}) - \nabla \cdot ((H_{1}n + H_{2}w)D_{H_{2}SiF_{6}} \cdot \nabla c_{H_{2}SiF_{6}}) + (H_{1} \cdot S_{1}^{\star}(1 - n) + H_{2})E_{4}c_{M_{1}}c_{H_{2}SiF_{6}} - \sum_{\text{mineral}=1}^{3} \frac{\delta_{i+4}}{\delta_{i}}(E_{i}c_{M_{i}}c_{\text{HF}}(H_{1} \cdot S_{i}^{\star}(1 - n) + H_{2})) = 0,$$
(A.13)

$$\partial_t ((1-n)c_{M_1}) + M_{HF} S_1^* c_{M_1} (1-n)\beta_1 E_1 c_{HF} / \rho_{M_1} + M_{H_2 SiF_6} S_1^* c_{M_1} (1-n)\beta_4 E_4 c_{H_2 SiF_6} / \rho_{M_1} = 0,$$
(A.14)

$$\partial_t ((1-n)c_{M_2}) + M_{HF} S_2^* c_{M_2} (1-n)\beta_2 E_2 c_{HF} / \rho_{M_2} = 0, \qquad (A.15)$$

$$\partial_t (nc_{M_3}) + M_{HF} S_3^* c_{M_3} n \beta_3 E_3 c_{HF} / \rho_{M_3} - M_{H_2 SiF_6} S_1^* c_{M_1} (1-n) \beta_4 E_4 c_{H_2 SiF_6} / \rho_{M_1} (\delta_8 M_{M_3} / M_{M_1}) = 0.$$
(A.16)

The boundary conditions can be specified as,

$$\begin{cases} \boldsymbol{u} = \hat{\boldsymbol{u}}, \text{ on } \partial \Omega_{\boldsymbol{u}} \\ p = \hat{p}, \text{ on } \partial \Omega_{p} \\ c_{HF} = \hat{c}_{HF}, \text{ on } \partial \Omega_{c_{HF}} \\ c_{H_{2}SiF_{6}} = \hat{c}_{H_{2}SiF_{6}}, \text{ on } \partial \Omega_{c_{H_{2}SiF_{6}}}; \\ c_{M_{1}} = \hat{c}_{M_{1}}, \text{ on } \partial \Omega_{c_{M_{1}}} \\ c_{M_{2}} = \hat{c}_{M_{2}}, \text{ on } \partial \Omega_{c_{M_{2}}} \\ c_{M_{3}} = \hat{c}_{M_{3}}, \text{ on } \partial \Omega_{c_{M_{3}}} \end{cases}; \begin{cases} \boldsymbol{\sigma} \cdot \boldsymbol{n} = \hat{\boldsymbol{t}}, \text{ on } \partial \Omega_{\boldsymbol{t}} \\ -\boldsymbol{w} \cdot \boldsymbol{n} = \hat{\boldsymbol{w}}, \text{ on } \partial \Omega_{\boldsymbol{w}} \\ q_{HF} \cdot \boldsymbol{n} = \hat{q}_{HF}, \text{ on } \partial \Omega_{q_{HF}} \\ q_{H_{2}SiF_{6}} \cdot \boldsymbol{n} = \hat{q}_{H_{2}SiF_{6}}, \text{ on } \partial \Omega_{q_{H_{2}SiF_{6}}} . \end{cases}$$
(A.17)

where  $\boldsymbol{n}$  is the unit normal vector on the boundary  $\partial\Omega$ , which is assigned outward-oriented as positive. Eq. (A.17)(1) are the Dirichlet boundaries while Eq. (A.17)(2) are the Neumann boundaries, which are satisfying,

$$\partial \Omega = \overline{\partial \Omega_{u} \cup \partial \Omega_{t}} = \overline{\partial \Omega_{p} \cup \partial \Omega_{w}}$$

$$= \overline{\partial \Omega_{c_{HF}} \cup \partial \Omega_{q_{c_{HF}}}} = \overline{\partial \Omega_{c_{H_{2}SiF_{6}}} \cup \partial \Omega_{q_{c_{H_{2}SiF_{6}}}}}$$

$$= \overline{\partial \Omega_{c_{M_{1}}} \cup \partial \Omega_{q_{c_{M_{1}}}}} = \overline{\partial \Omega_{c_{M_{2}} \cup \partial \Omega_{q_{c_{M_{2}}}}}} = \overline{\partial \Omega_{c_{M_{3}}} \cup \partial \Omega_{q_{c_{M_{3}}}}}$$

$$(A.18)$$

$$= \overline{\partial \Omega_{c_{M_{1}}} \cup \partial \Omega_{q_{c_{M_{1}}}}} = \overline{\partial \Omega_{c_{M_{2}} \cup \partial \Omega_{q_{c_{M_{2}}}}}} = \overline{\partial \Omega_{c_{M_{3}}} \cup \partial \Omega_{q_{c_{M_{3}}}}}$$

$$= \partial \Omega_{c_{HF}} \cap \partial \Omega_{q_{c_{HF}}} = \partial \Omega_{c_{H_2SiF_6}} \cap \partial \Omega_{q_{c_{H_2SiF_6}}}$$

$$= \partial \Omega_{c_{M_1}} \cap \partial \Omega_{q_{c_{M_1}}} = \partial \Omega_{c_{M_2} \cap \partial \Omega_{q_{c_{M_2}}}} = \partial \Omega_{c_{M_3}} \cap \partial \Omega_{q_{c_{M_3}}}$$
(A.19)

The boundary condition for the phase field as,

$$\phi = 1.0; \ \nabla \phi \cdot \boldsymbol{n} = 0, \tag{A.20}$$

which is assigned the Dirichlet and Neumann boundary of the initial cracks (notches). The initial conditions of the field equations are as,

$$u = u_0; \ p = p_0;$$

$$c_{HF} = c_{0,HF}; \ c_{H_2SiF_6} = c_{0,H_2SiF_6};$$

$$c_{M_1} = c_{0,M_1}; \ c_{M_2} = c_{0,M_2}; \ c_{M_3} = c_{0,M_3}.$$
(A.21)

Then, the trial spaces  $V_u$ ,  $V_p$ ,  $V_{\phi}$ ,  $V_{c_{\text{HF}}}$ ,  $V_{c_{\text{H}_2\text{SiF}_6}}$ ,  $V_{c_{M_1}}$ ,  $V_{c_{M_2}}$ ,  $V_{c_{M_3}}$  for solution variables are as follows:

$$V_{u} = \{\boldsymbol{u}: \Omega \to \mathbb{R}^{d} | \boldsymbol{u} \in [\boldsymbol{H}^{1}(\Omega)]^{d}, \boldsymbol{u}|_{\partial\Omega_{\boldsymbol{u}}} = \hat{\boldsymbol{u}}\},\$$

$$V_{p} = \{p: \Omega \to \mathbb{R} | p \in \boldsymbol{H}^{1}(\Omega), p|_{\partial\Omega_{p}} = \hat{p}\},\$$

$$V_{\phi} = \{\phi: \Omega \to \mathbb{R} | \phi \in \boldsymbol{H}^{1}(\Omega), \phi|_{\partial\Omega_{\phi}} = \hat{\phi}\},\$$

$$V_{c_{HF}} = \{c_{HF}: \Omega \to \mathbb{R} | c_{HF} \in \boldsymbol{H}^{1}(\Omega), c_{HF}|_{\partial\Omega_{c_{HF}}} = \hat{c}_{HF}\},\$$

$$V_{c_{H_{2}SiF_{6}}} = \{c_{H_{2}SiF_{6}}: \Omega \to \mathbb{R} | c_{H_{2}SiF_{6}} \in \boldsymbol{H}^{1}(\Omega), c_{H_{2}SiF_{6}}|_{\partial\Omega_{c_{H_{2}SiF_{6}}}} = \hat{c}_{H_{2}SiF_{6}}\},\$$

$$V_{c_{M_{1}}} = \{c_{M_{1}}: \Omega \to \mathbb{R} | c_{M_{1}} \in \boldsymbol{H}^{1}(\Omega), c_{M_{1}}|_{\partial\Omega_{c_{M_{1}}}} = \hat{c}_{M_{1}}\},\$$

$$V_{c_{M_{2}}} = \{c_{M_{2}}: \Omega \to \mathbb{R} | c_{M_{2}} \in \boldsymbol{H}^{1}(\Omega), c_{M_{2}}|_{\partial\Omega_{c_{M_{2}}}} = \hat{c}_{M_{2}}\},\$$

$$V_{c_{M_{3}}} = \{c_{M_{3}}: \Omega \to \mathbb{R} | c_{M_{3}} \in \boldsymbol{H}^{1}(\Omega), c_{M_{3}}|_{\partial\Omega_{c_{M_{3}}}} = \hat{c}_{M_{3}}\}.$$

where d = 1, 2, 3 is dimension,  $H^1(\Omega)$  denotes the Sobolev space of order 1. Thus, we further give the corresponding admissible shape function spaces of Eq. (A.22),

$$\begin{split} V_{\eta} &= \{ \boldsymbol{\eta} : \Omega \to \mathbb{R}^{d} | \boldsymbol{\eta} \in [\boldsymbol{H}^{1}(\Omega)]^{d}, \boldsymbol{\eta}|_{\partial\Omega_{\eta}} = \hat{\mathbf{0}} \}, \\ V_{\xi} &= \{ \xi : \Omega \to \mathbb{R} | \xi \in \boldsymbol{H}^{1}(\Omega), \xi |_{\partial\Omega_{\xi}} = 0 \}, \\ V_{\omega} &= \{ \omega : \Omega \to \mathbb{R} | \omega \in \boldsymbol{H}^{1}(\Omega), \omega |_{\partial\Omega_{\omega}} = 0 \}, \\ V_{\zeta_{c_{HF}}} &= \{ \zeta_{c_{HF}} : \Omega \to \mathbb{R} | \zeta_{c_{HF}} \in \boldsymbol{H}^{1}(\Omega), \zeta_{c_{HF}} |_{\partial\Omega_{\zeta_{c_{HF}}}} = 0 \}, \\ V_{\zeta_{c_{H2}SiF6}} &= \{ \zeta_{c_{H2}SiF6} : \Omega \to \mathbb{R} | \zeta_{c_{H2}SiF6} \in \boldsymbol{H}^{1}(\Omega), \zeta_{c_{H2}SiF6} |_{\partial\Omega_{\zeta_{c_{H2}SiF6}}} = 0 \}, \\ V_{\zeta_{c_{M_{1}}}} &= \{ \zeta_{c_{M_{1}}} : \Omega \to \mathbb{R} | \zeta_{c_{M_{1}}} \in \boldsymbol{H}^{1}(\Omega), \zeta_{c_{M_{1}}} |_{\partial\Omega_{\zeta_{c_{M_{1}}}}} = 0 \}, \\ V_{\zeta_{c_{M_{2}}}} &= \{ \zeta_{c_{M_{2}}} : \Omega \to \mathbb{R} | \zeta_{c_{M_{2}}} \in \boldsymbol{H}^{1}(\Omega), \zeta_{c_{M_{2}}} |_{\partial\Omega_{\zeta_{c_{M_{2}}}}} = 0 \}, \\ V_{\zeta_{c_{M_{3}}}} &= \{ \zeta_{c_{M_{3}}} : \Omega \to \mathbb{R} | \zeta_{c_{M_{3}}} \in \boldsymbol{H}^{1}(\Omega), \zeta_{c_{M_{3}}} |_{\partial\Omega_{\zeta_{c_{M_{3}}}}} = 0 \}. \end{split}$$

We then use the standard weighted residual procedure. The problem we solve for the weak equations is to find  $\{\boldsymbol{u}, p, \phi, c_{\mathrm{HF}}, c_{\mathrm{H_2SiF_6}}, c_{\mathrm{M_1}}, c_{\mathrm{M_2}}, c_{\mathrm{M_3}}\} \in V_u \times V_p \times V_\phi \times V_{c_{\mathrm{HF}}} \times V_{c_{\mathrm{H_2SiF_6}}} \times V_{c_{\mathrm{M_1}}} \times V_{c_{\mathrm{M_2}}} \times V_{c_{\mathrm{M_3}}}$ , such that for all  $\{\boldsymbol{\eta}, \boldsymbol{\xi}, \omega, \zeta_{c_{\mathrm{HF}}}, \zeta_{c_{\mathrm{H_2SiF_6}}}, \zeta_{c_{\mathrm{M_1}}}, \zeta_{c_{\mathrm{M_2}}}, \zeta_{c_{\mathrm{M_3}}}\} \in V_\eta \times V_{\boldsymbol{\xi}} \times V_\omega \times V_{\zeta_{c_{\mathrm{HF}}}} \times V_{\zeta_{c_{\mathrm{H_2SiF_6}}}} \times V_{\zeta_{c_{\mathrm{M_1}}}} \times V_{\zeta_{c_{\mathrm{M_2}}}} \times V_{\zeta_{c_{\mathrm{M_3}}}}$ . The residual vectors are,

$$G_u = G_p = G_{\phi} = G_{c_{HF}} = G_{c_{H_2SiF_6}} = G_{c_{M_1}} = G_{c_{M_2}} = G_{c_{M_3}} = 0;$$
(A.24)

where:

$$G_{u} = -\int_{\Omega} \nabla \boldsymbol{\eta} : \boldsymbol{\sigma}' d\Omega + \int_{\Omega} \boldsymbol{\eta} \rho \cdot \boldsymbol{g} d\Omega + \int_{\Omega} \nabla \cdot \boldsymbol{\eta} g p d\Omega + \int_{\Omega} \boldsymbol{\eta} p \cdot \nabla g d\Omega + \int_{\partial \Omega_{t}} \boldsymbol{\eta} \cdot \hat{\boldsymbol{t}} d\partial_{\Omega_{u}}, \quad (A.25)$$

$$G_{p} = \int_{\Omega} \xi \chi_{R} \nabla \cdot \dot{\boldsymbol{u}} d\Omega + \int_{\Omega} \nabla \xi \cdot \boldsymbol{K} \cdot \nabla p d\Omega - \int_{\Omega} \nabla \xi \cdot \boldsymbol{K} \cdot \rho_{w} \boldsymbol{g} d\Omega - \int_{\Omega} q \xi d\Omega + \int_{\Omega} \tau_{STAB} d\Omega - \int_{\partial \Omega_{p}} \xi \hat{\boldsymbol{w}} d\partial_{\Omega_{p}},$$
(A.26)

$$G_{\phi} = \int_{\Omega} \omega (\mathcal{H} + \frac{G_c}{l_0} \phi) d\Omega + \int_{\Omega} G_c l_0 \nabla \omega \cdot \nabla \phi d\Omega$$
(A.27)

$$G_{c_{HF}} = \int_{\Omega} (H_1 n + H_2 w) \zeta_{c_{HF}} \nabla \dot{c}_{HF} d\Omega + \int_{\Omega} \nabla \zeta_{c_{HF}} \cdot \boldsymbol{D}_{HF} \cdot (H_1 n + H_2 w) \nabla c_{HF} d\Omega$$
$$- \int_{\Omega} \nabla \zeta_{c_{HF}} \cdot (H_1 n + H_2 w) \boldsymbol{F}^{\boldsymbol{n} + \frac{1}{2}} d\Omega - \int_{\Omega} q_{c_{HF}} \zeta_{c_{HF}} d\Omega$$
$$- \int_{\partial \Omega_{c_{HF}}} \zeta_{c_{HF}} \hat{q}_{c_{HF}} d\partial_{\Omega_{c_{HF}}}, \tag{A.28}$$

$$G_{c_{H_{2}SiF_{6}}} = \int_{\Omega} (H_{1}n + H_{2}w)\zeta_{c_{H_{2}SiF_{6}}} \nabla \dot{c}_{H_{2}SiF_{6}} d\Omega + \int_{\Omega} \nabla \zeta_{c_{H_{2}SiF_{6}}} \cdot \boldsymbol{D}_{H_{2}SiF_{6}} \cdot (H_{1}n + H_{2}w)\nabla c_{H_{2}SiF_{6}} d\Omega - \int_{\Omega} \nabla \zeta_{c_{H_{2}SiF_{6}}} \cdot (H_{1}n + H_{2}w)\boldsymbol{F}^{\boldsymbol{n}+\frac{1}{2}} d\Omega \qquad (A.29) - \int_{\partial\Omega_{c_{H_{2}SiF_{6}}}} \zeta_{c_{H_{2}SiF_{6}}} \hat{q}_{c_{H_{2}SiF_{6}}} d\partial_{\Omega_{c_{H_{2}SiF_{6}}}},$$

$$G_{c_{M_{1}}} = \int_{\Omega} (1-n)\zeta_{c_{M_{1}}} \cdot \dot{c}_{M_{1}} d\Omega + \int_{\Omega} \zeta_{c_{M_{1}}} M_{HF} S_{1}^{\star} c_{M_{1}} (1-n)\beta_{1} E_{1} c_{HF} / \rho_{M_{1}} d\Omega + \int_{\Omega} \zeta_{c_{M_{1}}} M_{H_{2}} S_{iF_{6}} c_{M_{1}} (1-n)\beta_{4} E_{4} c_{H_{2}} S_{iF_{6}} / \rho_{M_{1}} d\Omega,$$
(A.30)

$$G_{c_{M_2}} = \int_{\Omega} (1-n)\zeta_{c_{M_2}} \cdot \dot{c}_{M_2} d\Omega + \int_{\Omega} \zeta_{c_{M_2}} M_{HF} S_2^{\star} c_{M_2} (1-n)\beta_2 E_2 c_{HF} / \rho_{M_2} d\Omega, \quad (A.31)$$

$$G_{c_{M_3}} = \int_{\Omega} (1-n)\zeta_{c_{M_3}} \cdot \dot{c}_{M_3} d\Omega + \int_{\Omega} \zeta_{c_{M_3}} M_{HF} S_3^* c_{M_3} n\beta_3 E_3 c_{HF} / \rho_{M_3} d\Omega - \int_{\Omega} M_{H_2 SiF_6} S_1^* c_{M_1} (1-n)\beta_4 E_4 c_{H_2 SiF_6} / \rho_{M_1} (\delta_8 M_{M_3} / M_{M_1}) d\Omega.$$
(A.32)

We note that the source/sink terms of the residual formulas for  $c_{\rm HF}$  and  $c_{\rm H_2SiF_6}$  are not considered at this stage; we further illustrate this in Appendix A.4.

### A.3.2 Galerkin form

We then express the Galerkin form of the components of the matrices and the vectors. If we let  $N_u$ ,  $N_p$ ,  $N_{\phi}$ ,  $N_{c_{\text{HF}}}$ ,  $N_{c_{\text{H}_2\text{SiF}_6}}$ ,  $N_{c_{\text{M}_1}}$ ,  $N_{c_{\text{M}_2}}$ , and  $N_{c_{\text{M}_3}}$  be the shape functions of the unknown primary variables, and  $\eta$ ,  $\xi$ ,  $\omega$ ,  $\zeta_{c_{\text{HF}}}$ ,  $\zeta_{c_{\text{H}_2\text{SiF}_6}}$ ,  $\zeta_{c_{\text{M}_1}}$ ,  $\zeta_{c_{\text{M}_2}}$ , and  $\zeta_{c_{\text{M}_3}}$  be the nodal values of the corresponding test functions, the approximations are as follows:

$$\begin{cases} \boldsymbol{u} \approx \boldsymbol{u}^{h} = \boldsymbol{N}_{u}\boldsymbol{u} \\ p \approx p^{h} = \boldsymbol{N}_{p}p \\ c_{HF} \approx c_{HF}^{h} = \boldsymbol{N}_{c_{HF}}c_{HF} \\ c_{H_{2}SiF_{6}} \approx c_{H_{2}SiF_{6}}^{h} = \boldsymbol{N}_{c_{H_{2}SiF_{6}}}c_{H_{2}SiF_{6}}c_{H_{2}SiF_{6}}; \end{cases} \begin{cases} \boldsymbol{\eta} \approx \boldsymbol{\eta}^{h} = \boldsymbol{N}_{\eta}\boldsymbol{\eta} \\ \boldsymbol{\xi} \approx \boldsymbol{\xi}^{h} = \boldsymbol{N}_{\boldsymbol{\xi}}\boldsymbol{\xi} \\ \boldsymbol{\zeta}_{c_{HF}} \approx \boldsymbol{\zeta}_{c_{HF}}^{h} = \boldsymbol{N}_{\boldsymbol{\zeta}_{c_{HF}}}\boldsymbol{\zeta}_{c_{HF}} \\ \boldsymbol{\zeta}_{c_{H2}SiF_{6}} \approx \boldsymbol{\zeta}_{c_{H2}SiF_{6}}^{h} = \boldsymbol{N}_{\boldsymbol{\zeta}_{c_{H2}SiF_{6}}}\boldsymbol{\zeta}_{c_{H2}SiF_{6}} \\ \boldsymbol{\zeta}_{c_{H2}SiF_{6}} \approx \boldsymbol{\zeta}_{c_{H2}SiF_{6}}^{h} = \boldsymbol{N}_{\boldsymbol{\zeta}_{c_{H2}SiF_{6}}}\boldsymbol{\zeta}_{c_{H2}SiF_{6}} \\ \boldsymbol{\zeta}_{c_{H2}SiF_{6}} \approx \boldsymbol{\zeta}_{c_{H2}SiF_{6}}^{h} = \boldsymbol{N}_{\boldsymbol{\zeta}_{c_{H2}SiF_{6}}}\boldsymbol{\zeta}_{c_{H2}SiF_{6}} \\ \boldsymbol{\zeta}_{c_{M1}} \approx \boldsymbol{\zeta}_{c_{M1}}^{h} = \boldsymbol{N}_{\boldsymbol{\zeta}_{c_{M2}}}\boldsymbol{\zeta}_{c_{M1}} \\ \boldsymbol{\zeta}_{c_{M2}} \approx \boldsymbol{\zeta}_{c_{M1}}^{h} = \boldsymbol{N}_{\boldsymbol{\zeta}_{c_{M1}}}\boldsymbol{\zeta}_{c_{M1}} \\ \boldsymbol{\zeta}_{c_{M2}} \approx \boldsymbol{\zeta}_{c_{M2}}^{h} = \boldsymbol{N}_{\boldsymbol{\zeta}_{c_{M2}}}\boldsymbol{\zeta}_{c_{M2}} \\ \boldsymbol{\zeta}_{c_{M3}} \approx \boldsymbol{\zeta}_{c_{M3}}^{h} = \boldsymbol{N}_{\boldsymbol{\zeta}_{c_{M3}}}\boldsymbol{\zeta}_{c_{M3}} \end{cases}$$
(A.33)

The gradient and divergence of the shape functions are defined as below,

$$\boldsymbol{B}_i = \nabla \boldsymbol{N}_i; \ \boldsymbol{b}_i = \nabla \cdot \boldsymbol{N}_i, \tag{A.34}$$

where i denotes different field unknown variables. We then provide the detailed expressions for the matrices and vectors in the semi-discretization Eqs. (3.68)-(3.75).

$$\begin{split} \mathbf{K} &= -\int_{\Omega} \mathbf{B}_{u}^{T} \tilde{\mathbf{c}} \mathbf{B}_{u} d\Omega, \\ \mathbf{G} &= \int_{\Omega} \mathbf{b}_{u}^{T} g \mathbf{N}_{p} + \mathbf{N}_{u}^{T} \nabla g \mathbf{N}_{p} d\Omega, \\ \mathbf{H} &= \int_{\Omega} \mathbf{N}_{p}^{T} \chi_{R} \mathbf{b}_{u} d\Omega, \\ \mathbf{X} &= \int_{\Omega} [\mathbf{B}_{p}^{T} \mathbf{K} \mathbf{B}_{p} + \tau_{STAB} (\mathbf{N}_{p} - \bar{\mathbf{N}}_{p})^{T} (\mathbf{N}_{p} - \bar{\mathbf{N}}_{p})] d\Omega, \\ \mathbf{\kappa} &= \int_{\Omega} [\mathbf{N}_{\phi}^{T} (\frac{c_{c}}{l_{0}}) \mathbf{N}_{\phi} + \mathbf{B}_{\phi}^{T} (G_{c} l_{0}) \mathbf{B}_{\phi}] d\Omega, \\ \mathbf{S}_{1} &= \int_{\Omega} \mathbf{N}_{cM_{1}}^{T} (1 - n) \mathbf{N}_{cM_{1}} d\Omega, \\ \mathbf{T}_{1} &= \int_{\Omega} [\mathbf{N}_{cM_{1}}^{T} (M_{HF} S_{1}^{*} (1 - n) \beta_{1} E_{1} c_{HF} |_{n} + M_{H_{2} SiF_{6}} (1 - n) \beta_{4} E_{4} c_{H_{2} SiF_{6}} |_{n}) / \rho_{M_{1}} \mathbf{N}_{cM_{1}}] d\Omega, \\ \mathbf{S}_{2} &= \int_{\Omega} \mathbf{N}_{cM_{2}}^{T} (1 - n) \mathbf{N}_{cM_{2}} d\Omega, \\ \mathbf{T}_{2} &= \int_{\Omega} \mathbf{N}_{cM_{2}}^{T} (M_{HF} S_{2}^{*} (1 - n) \beta_{2} E_{2} c_{HF} |_{n} / \rho_{M_{2}}) \mathbf{N}_{cM_{2}} d\Omega, \\ \mathbf{S}_{3} &= \int_{\Omega} \mathbf{N}_{cM_{3}}^{T} (1 - n) \mathbf{N}_{cM_{3}} d\Omega, \\ \mathbf{T}_{3} &= \int_{\Omega} \mathbf{N}_{cM_{3}}^{T} (M_{HF} S_{3}^{*} n \beta_{3} E_{3} c_{HF} |_{n} / \rho_{M_{3}}) \mathbf{N}_{cM_{3}} d\Omega, \end{split}$$

$$\begin{split} \mathbf{E}_{1} &= \int_{\Omega} \mathbf{N}_{c_{HF}}^{T} (H_{1}n + H_{2}w) \mathbf{N}_{c_{HF}} d\Omega, \\ \mathbf{Q}_{1} &= \int_{\Omega} [\mathbf{B}_{c_{HF}}^{T} \mathbf{D}_{HF} \cdot (H_{1}n + H_{2}w) \mathbf{B}_{c_{HF}} + \mathbf{B}_{c_{HF}}^{T} (H_{1}n + H_{2}w) \tilde{\mathbf{F}}^{n+\frac{1}{2}} \mathbf{B}_{c_{HF}}] d\Omega, \\ \mathbf{E}_{2} &= \int_{\Omega} \mathbf{N}_{c_{H_{2}SiF_{6}}}^{T} (H_{1}n + H_{2}w) \mathbf{N}_{c_{H_{2}SiF_{6}}} d\Omega, \\ \mathbf{Q}_{2} &= \int_{\Omega} [\mathbf{B}_{c_{H_{2}SiF_{6}}}^{T} \mathbf{D}_{H_{2}SiF_{6}} \cdot (H_{1}n + H_{2}w) \mathbf{B}_{c_{H_{2}SiF_{6}}} + \mathbf{B}_{c_{H_{2}SiF_{6}}}^{T} (H_{1}n + H_{2}w) \tilde{\mathbf{F}}^{n+\frac{1}{2}} \mathbf{B}_{c_{H_{2}SiF_{6}}}] d\Omega, \\ \mathbf{R}_{u} &= \int_{\partial\Omega} - \mathbf{N}_{u}^{T} \hat{t} dS - \int_{\Omega} \mathbf{N}_{u}^{T} \rho g d\Omega, \\ \mathbf{R}_{v} &= \int_{\Omega} [\mathbf{B}_{p}^{T} (\mathbf{K} \rho_{w} g) + \mathbf{N}_{p}^{T} \hat{s}] d\Omega + \int_{\partial\Omega} \mathbf{N}_{p}^{T} \hat{\omega} dS, \\ \mathbf{R}_{\phi} &= -\int_{\Omega} \mathbf{N}_{\phi}^{T} H d\Omega, \\ \mathbf{R}_{c_{M_{1}}} &= \mathbf{0}, \\ \mathbf{R}_{c_{M_{2}}} &= \mathbf{0}, \\ \mathbf{R}_{c_{M_{3}}} &= \int_{\Omega} \mathbf{N}_{c_{M_{3}}}^{T} M_{H_{2}SiF_{6}} S_{1}^{*} c_{M_{1}} |_{n} (1 - n) \beta_{4} E_{4} c_{H_{2}SiF_{6}} |_{n} / \rho_{M_{1}} (\delta_{8} M_{M_{3}} / M_{M_{1}}) d\Omega, \\ \mathbf{R}_{c_{HF}} &= \int_{\Omega} \mathbf{N}_{c_{HF}}^{T} q_{c_{HF}} d\Omega + \int_{\partial\Omega} \mathbf{N}_{c_{HF}}^{T} \hat{q}_{c_{HF}} d\Omega, \\ \mathbf{R}_{c_{H_{2}SiF_{6}}} &= \int_{\partial\Omega} \mathbf{N}_{c_{H_{2}SiF_{6}}}^{T} \hat{q}_{c_{H_{2}SiF_{6}}} d\Omega. \end{split}$$

where  $\tilde{c}$  indicates tangential stiffness, which is defined here as  $g(\phi, \phi^{chem})^e$ .  $\tilde{F}^{n+\frac{1}{2}}$  is defined as A.4.

### A.4 combined a Taylor-Galerkin scheme for advective transport and a Runge–Kutta fourth-order scheme for the source term

For the advective term in Eqs. (3.41), (3.42), or (3.71), we adopt a two-step Taylor-Galerkin algorithm. This method is based on a Taylor series expansion in time of the solution at time step n. Here, we present the general approach to dealing with the advection term and denote  $c_i$  as the general concentration of a species. Then, we have, Then, we have,

$$c_i^{n+\frac{1}{2}} = c_i^n + \frac{\Delta t}{2} (\frac{\partial c_i}{\partial t})^n, \tag{A.37}$$

$$\left(\frac{\partial c_i}{\partial t}\right)^n = -\nabla \cdot \boldsymbol{F}_i^n,\tag{A.38}$$

where the concentration flux is defined as  $F_i = (vc_i)^n$ . consequently,

$$c_i^{n+\frac{1}{2}} = c_i^n + \frac{\Delta t}{2} (-\nabla \cdot F_i^n).$$
 (A.39)

Then, we can obtain flux at time  $n + \frac{1}{2}$  and use them in the second step:

$$c_i^{n+1} = c_i^n + \Delta t \left(\frac{\partial c_i}{\partial t}\right)^{n+\frac{1}{2}} = c_i^n - \Delta t \nabla \cdot \boldsymbol{F}_i^{n+\frac{1}{2}}.$$
 (A.40)

As for the  $\nabla F_i^{n+\frac{1}{2}}$ , we give the below derivations.

$$\widetilde{F}_{i}^{n+\frac{1}{2}} = \frac{\partial F_{i}^{n+\frac{1}{2}}}{\partial c_{i}} = \boldsymbol{v}^{n+\frac{1}{2}} \frac{\partial c_{i}^{n+\frac{1}{2}}}{\partial c_{i}};$$
(A.41)

$$\frac{\partial c_i^{n+\frac{1}{2}}}{\partial c_i} = \frac{dc_i^n}{dc_i} - \frac{\Delta t}{2} \nabla \cdot \frac{\boldsymbol{F_i}^n}{\partial c_i}; \tag{A.42}$$

$$\nabla \cdot \frac{F_i^n}{\partial c_i} = \nabla \cdot (\boldsymbol{v})^n; \tag{A.43}$$

$$\nabla \cdot (\boldsymbol{v})^n = \nabla \cdot (-\frac{\kappa}{\nu} \nabla p)^n.$$
(A.44)

As we discuss in Section 3.7.2, the source term is separated to solve as an ordinary differential equation (ODE). Here, We employ a Runge-Kutta fourth-order accurate

scheme to solve it. The separated ODE is,

$$\frac{dc_i}{dt} = S(c_i),\tag{A.45}$$

The general form of the Runge-Kutta algorithm is,

$$c_i^{n+1} = c_i^n + \Delta \sum_{k=1}^k \beta^k S(c_i^k),$$
 (A.46)

where  $\beta^k$  is the corresponding coefficient. Regarding the fourth-order problem, we expand the above general formulation as below,

$$c_1 = c_i^n; \tag{A.47}$$

$$c_2 = c_i^n + \frac{1}{2}\Delta t S(c_1);$$
 (A.48)

$$c_3 = c_i^n + \frac{1}{2}\Delta t S(c_2); \tag{A.49}$$

$$c_4 = c_i^n + \Delta t S(c_3). \tag{A.50}$$

So, finally we can update the concentration as,

$$c_i^{n+1} = c_i^n + \frac{\Delta t}{6} [S(c_1) + 2S(c_2) + 2S(c_3) + S(c_4)].$$
(A.51)

### A.5 Derivation of partial differential formulations

We derive the specific formulations for the derivations of Eq.  $(4.42) \sim (4.46)$  and Eq.  $(4.52) \sim (4.56)$ . The relevant derivations of those equations are,

$$\frac{\partial \tilde{M}}{\partial p} = \frac{M^2}{\tilde{M}} (1 - \tilde{\alpha}) \frac{1}{p_d}; \tag{A.52}$$

$$\frac{\partial \tilde{M}}{\partial p_d} = -\frac{M^2}{\tilde{M}} (1 - \tilde{\alpha}) \frac{p}{p_d^2}; \tag{A.53}$$

$$\frac{\partial p_d}{\partial p_c} = 1; \tag{A.54}$$

$$\frac{\partial p_d}{\partial p_b} = -b; \tag{A.55}$$

$$\frac{\partial_p \mathcal{F}}{\partial p_c} = \frac{\partial_p \mathcal{F}}{\partial p_d} \frac{\partial p_d}{\partial p_c} = -1 + 2\frac{q^2}{p_d^2} \frac{M^2}{\tilde{M}^4} (1 - \tilde{\alpha}) - 8\frac{q^2 p}{p_d^3} (1 - \tilde{\alpha})^2 \frac{M^4}{\tilde{M}^6};$$
(A.56)

$$\frac{\partial_p \mathcal{F}}{\partial p_b} = \frac{\partial_p \mathcal{F}}{\partial p_d} \frac{\partial p_d}{\partial p_b} + \frac{\partial_p \mathcal{F}}{\partial p_b} = -2 - \left[-1 + 2\frac{q^2}{p_d^2} \frac{M^2}{\tilde{M}^4} (1 - \tilde{\alpha}) - 8\frac{q^2 p}{p_d^3} \frac{M^4}{\tilde{M}^6} (1 - \tilde{\alpha})^2\right] b; \quad (A.57)$$

$$\frac{\partial_q \mathcal{F}}{\partial p_c} = 4 \frac{qp}{p_d^2} \frac{M^2}{\tilde{M}^4} (1 - \alpha); \tag{A.58}$$

$$\frac{\partial_q \mathcal{F}}{\partial p_b} = 4b \frac{qp}{p_d^2} \frac{M^2}{\tilde{M}^4} (1 - \tilde{\alpha}); \tag{A.59}$$

$$\frac{\partial \mathcal{F}}{\partial p_c} = \frac{\partial \mathcal{F}}{\partial p_d} \frac{\partial p_d}{\partial p_c} = 2 \frac{q^2 p}{p_d^2} \frac{M^2}{\tilde{M}^4} (1 - \tilde{\alpha}) + p_b - p; \tag{A.60}$$

$$\frac{\partial \mathcal{F}}{\partial p_b} = \frac{\partial \mathcal{F}}{\partial p_b} + \frac{\partial \mathcal{F}}{\partial p_d} \frac{\partial p_d}{\partial p_b} = -2b \frac{q^2 p}{p_d^2} \frac{M^2}{\tilde{M}^4} (1 - \tilde{\alpha}) + b(p - p_b); \tag{A.61}$$

$$\frac{\partial p_c}{\partial \epsilon_v^e} = \frac{\partial p_c}{\partial \epsilon_v^{e,tr}} = -p_{c,n} \frac{1}{\hat{\lambda} - \tilde{k}} e^{-\left(\frac{\epsilon_v^{e,tr} - \epsilon_{v,n}^e}{\hat{\lambda} - \tilde{k}}\right)};$$
(A.62)

$$\frac{\partial p_b}{\partial \epsilon_v^e} = \frac{\partial p_b}{\partial \epsilon_v^{e,tr}} = -\frac{2}{3} (1 - \phi_n) u p_{b,0} e^{-u \sqrt{\frac{2(\epsilon_v^{e,tr} - \epsilon_{v,n}^e)^2 - 9(\epsilon_s^{e,tr} - \epsilon_{s,n}^e)^2}{6}}}{\chi - \frac{1}{(\epsilon_v^{e,tr} - \epsilon_{v,n}^e)}}$$
(A.63)

$$\sqrt{\frac{2(\epsilon_v^{e,tr} - \epsilon_{v,n}^e)^2 - 9(\epsilon_s^{e,tr} - \epsilon_{s,n}^e)^2}{6}} \sqrt{\frac{2(\epsilon_v^{e,tr} - \epsilon_{s,n}^e)^2}{6}}$$
(11.00)

$$\frac{\partial p_c}{\partial \epsilon_s^e} = \frac{\partial p_c}{\partial \epsilon_s^{e,tr}} = 0; \tag{A.64}$$

$$\frac{\partial p_b}{\partial \epsilon_s^e} = \frac{\partial p_b}{\partial \epsilon_s^{e,tr}} = 3(1 - \phi_n) u p_{b,0} e^{-u \sqrt{\frac{2(\epsilon_v^{e,tr} - \epsilon_{v,n}^e)^2 - 9(\epsilon_s^{e,tr} - \epsilon_{s,n}^e)^2}{6}}}{\frac{1}{\sqrt{\frac{2(\epsilon_v^{e,tr} - \epsilon_{v,n}^e)^2 - 9(\epsilon_s^{e,tr} - \epsilon_{s,n}^e)^2}{6}}} (\epsilon_s^{e,tr} - \epsilon_{s,n}^e);$$
(A.65)

### A.6 components of matrix $D^e$

We also note that the components of the hyperelasticity are,

$$D_{11}^{e} = K = -\frac{p}{\tilde{k}} = -\frac{p_0}{\tilde{k}} [1 + \frac{3t}{2\tilde{\kappa}} (\epsilon_s^{e2})] e^{(-\frac{\epsilon_v^e - \epsilon_v^e}{\tilde{\kappa}} - \epsilon_v^e)};$$
(A.66)

$$D_{12}^e = \frac{3pt\epsilon_s^e}{\tilde{k}}e^{\left(-\frac{\epsilon_v^e - \epsilon_{v0}^e}{\tilde{\kappa}}\right)};\tag{A.67}$$

$$D_{21}^e = D_{12}^e; (A.68)$$

$$D_{22}^{e} = 3G = 3[G_0 - tp_0 e^{(-\frac{\epsilon_v^e - \epsilon_{v0}^e}{\tilde{\kappa}})}]\epsilon_s^e.$$
(A.69)

### A.7 components of matrix A

Finally, the matrix  $\mathcal{B}$  is the inverse matrix of Jacobin  $\mathcal{A}$ . The expressions for each terms can be referred to Appendix A.5. In this case, we list all of the components of the Jacobin matrix as,

$$A_{11} = 1 + \Delta \phi [G_{11} + \frac{\partial_p \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_v^e} + \frac{\partial_p \mathcal{F}}{\partial p_d} (\frac{\partial p_d}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_v^e} + \frac{\partial p_d}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_v^e})];$$
(A.70)

$$A_{12} = \Delta \phi [G_{12} + \frac{\partial_p \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_s^e} + \frac{\partial_p \mathcal{F}}{\partial p_d} (\frac{\partial p_d}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_s^e} + \frac{\partial p_d}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_s^e})];$$
(A.71)

$$A_{13} = \partial_p \mathcal{F}; \tag{A.72}$$

$$A_{21} = \Delta \phi [(G_{21} + \frac{\partial_q \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_v^e} + \frac{\partial_q \mathcal{F}}{\partial p_d} (\frac{\partial p_d}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_v^e} + \frac{\partial p_d}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_v^e})];$$
(A.73)

$$A_{22} = 1 + \Delta\phi[(G_{22} + \frac{\partial_q \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_s^e} + \frac{\partial_q \mathcal{F}}{\partial p_d} (\frac{\partial p_d}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_s^e} + \frac{\partial p_d}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_s^e})];$$
(A.74)

$$A_{23} = \partial_q F; \tag{A.75}$$

$$A_{31} = \frac{\partial \mathcal{F}}{\partial p} D_{11}^e + \frac{\partial \mathcal{F}}{\partial q} D_{21}^e + \frac{\partial \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_v^e} + \frac{\partial \mathcal{F}}{\partial p_d} (\frac{\partial p_d}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_v^e} + \frac{\partial p_d}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_v^e});$$
(A.76)

$$A_{32} = \frac{\partial \mathcal{F}}{\partial p} D_{12}^e + \frac{\partial \mathcal{F}}{\partial q} D_{22}^e + \frac{\partial \mathcal{F}}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_s^e} + \frac{\partial \mathcal{F}}{\partial p_d} (\frac{\partial p_d}{\partial p_c} \frac{\partial p_c}{\partial \epsilon_s^e} + \frac{\partial p_d}{\partial p_b} \frac{\partial p_b}{\partial \epsilon_s^e});$$
(A.77)

$$A_{33} = 0. (A.78)$$