

UNIVERSITY OF TWENTE.

Faculty of Engineering Technology

Geological storage of CO₂: Influence of mineral dissolution on the cap rock stabilit. A discrete element approach

> Luca Pecoriello M.Sc. Thesis June 2016

> > Supervisors: Dr.Ir. R.S. de Graaf Dr. V. Magnanimo Dr.Ir. U.F.A. Karim Dr.Ir. H.L. Ter Huerne

Civil Engineering and Management Faculty of Engineering Technology, University of Twente P.O. Box 217 7500 AE Enschede The Netherlands

Abstract

Geologic storage is considered the most viable option to reduce CO_2 net emissions in the atmosphere, as it enhances its sink deep underground even for centuries. Storage in competent porous formations requires sufficient voids capacity and a tightly sealed impermeable cap rock that remains stable at high temperature and pressure. Given that CO_2 in its supercritical phase is a solvent, gradual dissolution will result in a proportion of the parent rock at micro (minerals and voids) scale, and macro, grain-to-grain contact scale. The reduced skeleton contact areas between the grains can result in a loss of bearing capacity of the porous media, that can lead to destabilization of the cap rock.

This class of multi-scale problems in soil mechanics is investigated using the DEM (Discrete Element Method). This investigation focuses on modeling with the DEM, the gradual grain dissolution of idealized Silica-Quartz (SiO₂) and Calcium-Oxide (CaO)-rich porous rocks, that can be found in a CO_2 - storage reservoir. Different kinetics of dissolution for the samples are considered while the lithostatic load is constantly present. The dissolution is modeled as shrinkages of particles, in which different shrinkages are considered. A new DEM-based methodology is first depicted. Its main advantages are simplicity in usage, real physical inputs, economical feasibility, and low-cost repeatability. A series of DEM simulations are performed applying this methodology, creating numerical samples that represent the idealized reservoir. Numerical data obtained by DEM simulations, give insights about the most likely failure mechanism of the caprock due to excessive mineral dissolution.

Declaration of Authorship

The research work described and reported in this thesis has been completely solely by Luca Pecoriello, under the supervision of Dr.Ir. R.S. de Graaf, Dr. V. Magnanimo, Dr.Ir. U.F.A. Karim and Dr.Ir. H.L. Ter Huerne. The Author, hereby confirms that:

- 1. Where it was needed to consult published works of others, this is always clearly attributed.
- 2. Where it was needed to quote from the work of others, the source is given.
- 3. All main source of help are acknowledged.

ŀ	٩r	ו	d	
-				,

The Author and M.Sc. Stude Signature	ent: Luca Pecoriello on date:	
Dr. Ir. R.S. de Graaf Signature	on date:	
Dr. V. Magnanimo		
Signature	on date:	
Dr.Ir. U.F.A. Karim		
Signature	on date:	
Dr.Ir. H.L. Ter Huerne		
Signature	on date:	

Confirm the originality and novelty of the research contained in this manuscript

Please note the following terms and conditions of use:

- 1. This work is protected by copyright and other intellectual property rights, which are retained by the Author of this thesis, unless the otherwise is stated.
- 2. A copy can be download for personal non-commercial research or study, without prior permission.
- 3. This M.Sc. Thesis cannot be reproduced or quoted extensively from without first obtaining permission in writing from the Author.
- 4. The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the Author.
- 5. When referring to this work, full bibliographic details, including the Author, Title, awarding institution and date of the thesis must be given.

Acknowledgments

My first thanks goes to my family, for the incredible support I have received during this experience in the Netherlands. You all have been a tremendous drive to stand up in times of distress. Secondly, I would like to thank my friends just for being my friends, you know who you are. Third, a thank you goes to my supervisors for allowing my research.

Il mio primo ringraziamento va alla mia famiglia per l'incredibile supporto ricevuto durante questa esperienza in Olanda. Il vostro supporto e' stato sempre la chiave di volta nei momenti piu' difficili. Secondo, vorrei ringraziare i miei amici, sapete chi siete. Terzo, un ringraziamento ai miei supervisor per avermi lasciato svolgere la mia ricerca.

Mijn eerste dank gaat uit naar al mijn familie, voor de ongelooflijke steun die ik tijdens deze master in Nederland ontvangen. Uw steun en aanwezigheid (hoewel vaak virtueel), is een hoeksteen in de meest moeilijke tijden. Ten tweede zou ik graag mijn vrienden willen bedanken, je weet wie je bent. Ten derde, een bedankje gaat naar mijn begeleiders om mij een zeer innovatief onderzoek uit te laten voeren.

Background Information

University of Twente

The University of Twente is a modern, entrepreneurial university, leading in the area of new technologies and a catalyst for change, innovation and progress in society: the very strength of our university lies in its capacity to combine these characteristics together. The University of Twente is currently working on future technologies at 360 degrees, including: ICT, biotechnology and nanotechnology for which behavioural and social science research are essential. The most interesting and relevant innovations take place at the cutting edge of these technologies and their impact on humanity and societies. The institutes combine scientific excellence with a keen eye for commercial knowledge valorization (the transformation of complex knowledge into economic activity) and social applications: they are successful in generating spin-off businesses. Science is all about talent. It is in line with the academic and entrepreneurial goals of the University of Twente, to be part of a research related to an upcoming technology such as Carbon Capture and Storage and Geologic Sequestration of CO_2 . By being part of this technology, the University of Twente has the possibility of positioning itself among the top innovative universities worldwide.

Two department of the University of Twente are addressed within this manuscript:

Construction Management and Engineering Department (CME)

The CME faculty is dedicated to educate the future generation of civil engineers. In our program, CME M.Sc. courses acknowledge that today's problems require integrated solutions. The diverse background of the CME department creates a perfect environment to teach students to solve complex civil engineering projects because the future civil engineering practice is increasingly multifunctional. Worldwide the Civil Engineering Program is recognized for its approach on project-based learning. Not only do students benefit from interaction with practice they learn how to adapt theoretical insights and tools in practice. Close ties to industry secure a demand-driven perspective of the program. It also gives students access to interesting topics for research assignments and excellent career opportunities.

Multiscale Mechanics Group (MSM)

The Multiscale Mechanics Group (MSM) of the University of Twente studies several topics of condensed matter physics, such as granular materials and powders, micro-fluidic systems and self-healing materials. In general, our research approach consists in developing models of complex materials that capture the physics at every relevant length scale. I believe that these two departments should be involved and have interest in developing a research within the topic of Carbon Capture and Storage and more into details, within geologic sequestration of CO_2 .

List of acronyms

For a smooth and more pleasant reading, quantities and symbols should be clear and unique. Throughout this report, the reader will find notations or abbreviations, to express various physical and numerical quantities, but nomenclature is not always unique. Therefore, in each of the following tables, the adopted symbols and units of measurements are collected. The column named "SYMBOL", represents the notation adopted in this report, while the column "AL." (standing for "Alternative"), collects other major nomenclatures available for the same quantity.

Granular Material

Granular Material - Notation								
ΝΑΜΕ	Symbol	AL.	Unit					
Young's Modulus	Y	E	Pa					
Poisson's ratio	ν	-	[Adim]					
Volume fraction	ϕ	V_{Fract}	[Adim]					
Porosity	n	-	[Adim]					
Void Ratio	е	-	[Adim]					
Particle's density	ρ	-	[Mass/L ³]					
Material's (bulk) density	$ ho_{bulk}$	-	[Mass/L ³]					
Stress	[σ]	-	Pa					
Strain	[<i>ϵ</i>]	-	Pa					

In the following table 1, the granular material-related symbols adopted in this research are shown.

Table 1: Granular material-related symbols adopted in this research

DEM-Simulation

In the following table 2, the mathematical-related symbols adopted in this research are shown.

Simula	ation - Notatic	on	
ΝΑΜΕ	Symbol	AL.	Unit
Time step interval	Δt	dt	[Time]
Particle overlap	δ	Δ	[Length]
Damping coefficient	γ	γ_n	[N*Time/L]
Relative displacement vector	Δ	-	[-]
Damping ratio	θ	-	[-]
Particle mass	m	-	[-]
Stiffness tensor	С	[K]	[-]
Generalized force vector	F	-	[-]
Force vector	f	\overrightarrow{f}	[Newton]
Generalized mass matrix	М	[M]	[mass]
Contact normal	n	n	[-]
Contact stiffness matrix	S ^c	[k]	[Newton/L]
Stiffness coefficient	а	k (ev. α)	[-]
Kinetic Energy	E_{Kin}	Kin	[Joule]
Branch vector	I_b	b	[Length]
Number of timesteps	N_T	Ν	[Adim]
Particle radius	r	-	[Length]
Total simulation time	Т	T_{f}	[Time]
Collision time	t_c	-	[Time]
Potential energy	E_{pot}	Pot, U	[Joule]
Volume	V	Vol	[L ³]
Acceleration vector	\ddot{x}	-	[-]
Velocity vector	\dot{x}	-	[-]
Position vector	Х	-	[-]

Table 2: DEM-Simulation-related symbols adopted in this research

Mathematical

In the following table 3, the mathematical-related symbols adopted in this research are shown.

Mathematical - Notation					
ΝΑΜΕ	Symbol				
Scalar product/matrix product					
Nabla operator	∇				
Dyadic product	\otimes				

Table 3: Mathematical-related symbols adopted in this research

(Geo) - Chemistry

In the following table 4, the chemical-related symbols adopted in this research are shown.

(Geo) - Chemistry - Notation						
ΝΑΜΕ	Symbol	Unit				
Kinetic Rate constant	k_m	$[mol m^{-2} s^{-1}]$				
Reactive surface area	А	[Length ²]				
Turnover frequency	λ_i	[1/time]				

Table 4: Chemical-related symbols adopted in this research

Geotechnical

In the following table 5, the geotechnical-related symbols adopted in this research are shown.

Geophysics - Notation						
ΝΑΜΕ	Symbol	Unit				
Depth	z	[L]				
Average soil density	$ ho_{soil}$	[kg/m ³]				
Lithostatic Load	σ_{Lith}	[Pa]				

Table 5: Geotechnical-related symbols adopted in this research

Contents

1	Intro	oduction 3
	1.1	From climate change to carbon storage 3
		1.1.1 Thesis goal and overview
	1.2	Thesis outline 8
2	The	oretical background 9
	2.1	CO ₂ geological storage
		2.1.1 Geological Reservoir
		2.1.2 Trapping mechanisms
	2.2	Long-term storage under mineral dissolution
		2.2.1 Dissolution
	2.3	Numerical simulation in CO_2 geological storage
3	Nun	nerical Methodology 17
	3.1	Introduction to discrete element method
		3.1.1 Equation of motion
		3.1.2 Contact forces
		3.1.3 Numerical specific aspects
		3.1.4 Relevant averaged output quantities
		3.1.5 Software
4	Sim	ulation Setup 27
	4.1	Modeling simplifications
		4.1.1 Assumptions
		4.1.2 Sample preparation
	4.2	Modeling the dissolution
5	Sim	ulation results 43
	5.1	Pre-failure behavior
		5.1.1 Averaged - Per- Cell - quantities
	5.2	Failure behavior
		5.2.1 Test case: Reduced box
	5.3	Failure mode: Unlimited accelerated shrinking
	5.4	Failure mode: Unlimited scaled shrinking 58

		5.4.1	Results								•		•	•		• •	 •				59
6	Con	clusio	ns and recomi	nenda	tior	าร														1	117
	6.1	Conclu	usion																		117
		6.1.1	Methodology																	•	117
		6.1.2	Failure analys	is																	120
	6.2	Recon	nmendations .								•		•	• •					•	•	123
Re	ferer	nces																		1	127
Aŗ	penc	dices																			
	6.3	Appen 6.3.1	dix: Coding . Script in LIGC	GHTS	 S: "L	 oad	erlı	 nfir	 nitel	Dis	sol	 ver			•	 	 •	· ·	•	•	132 132

Chapter 1

Introduction

1.1 From climate change to carbon storage

Our society is heavily dependent on fossil fuels, which supply about 81% of the primary energy worldwide [1]. They are used to produce about 67% of the world's electricity, of which coal, natural gas and oil contribute for circa 41%, 21% and 5%, respectively [2]. The constant growth of the global demand for energy services, together with the relative abundance of fossil fuels and the proven technologies for using them, suggests that fossil fuels will continue to be widely used until at least 2030 (Fig.1.1) [1].





The above raises concerns of climate destabilization. In fact, by burning more fossil fuels in order to generate energy, an increased quantity of greenhouse gases (GHG) is generated, polluting the atmosphere further more.

Among GHGs emitted, carbon-dioxide (CO₂) emissions have a dominant influence [4]. Previsions for the year 2100, suggest that, if no action is taken, the global average temperature can increase from 1.4° C (1990) to 5.8° C [1], leading to increasing precipitations, increased frequency of extreme climate events, the disruption of ecosystems, and the extinction of species. Therefore, in order to reduce the occurrence of these events, the stabilization or, ideally, reduction of CO_2 concentrations in the atmosphere, led to the development of three main ways to control global warming [1]:

- · Using fewer carbon intensive fuels
- · Improving energy efficiency, and
- · Carbon capture and sequestration (or storage) (CCS) through different means

The third option, CCS, is the most realistic, compared to options 1. and 2., since it allows industry to keep producing energy, whilst reducing the environmental impact [4]. Broadly speaking, CCS consists of capturing CO_2 from the atmosphere, followed by storing it in a reservoir where it can react with other materials, in order to trap it by creating stable compounds.

Among all means of conducting CCS, the most known is its injection and storage in geological reservoirs (underground), which takes the name of "geological sequestration" or " CO_2 geological sequestration (or storage), since the Earth's crust offers several options for storing the CO_2 . Specifically, CO_2 can be stored in [1]:

- Depleted oil and gas reservoirs. In particular, CO₂ storage can be combined with enhanced oil - or gas - recovery, an energy industry technique that consists of injecting CO₂ in a well in order to upstream almost the totality of the oil or gas contained in a reservoir.
- · Unused saline water-saturated reservoir rocks
- Unmineable coal seams
- · Basalts, oil shales and cavities

Although geological sequestration of CO_2 is nowadays considered a crucial technology in the long-term carbon abatement strategies of many countries and international organizations [5], securing such a large volume still requires a solid scientific foundation defining the coupled hydrological, geochemical and geomechanical processes that govern the longterm fate of CO_2 , which are not fully grasped.

As far as scientific lacks are present, geological storage of CO_2 can not upscale to largescale industry [6].

1.1.1 Thesis goal and overview

Within this M.Sc. Thesis, the student is interested in developing more soil micro-scale mechanics insights related to geological reservoirs used for geological storage of CO_2 . Knowledge from geochemistry is applied for an improved understanding of the geotechnical stability of a reservoir during long-term storage. For example, as reported by Kampmann [6], mineral-fluid contact under geologic reservoir condition, involving supercritical CO_2 is still poorly understood. It is known that the supercritical CO_2 can occupy very little volume compared to its fluid and gas phases, but it is well-known to be a very powerful solvent.

Therefore, the Student's interests are the following. The first goal is to unravel one aspect of the mineral-supercritical CO_2 contact under geological reservoir conditions, which is the dissolution of the porous media. In fact, CO_2 will be stored in the porous media of a geological reservoir, which will be then sealed by an impermeable layer called caprock. Since the sealing rock of the reservoir is laying on that porous media, excessive dissolution can change the stability of the cap rock itself and of the reservoir as a whole. As an approach able to describe micro-mechanical consequences for a geological reservoir undergoing dissolution enhance by supercritical CO_2 , is missing, the second goal is to establish a suitable numerical approach.

Approach and key focus areas The research question, that is desired to be answered is the following.

Can mineral dissolution in the long-term geological storage, affect the sealing capacity of the geological formation, under a geotechnical perspective?

As depicted in Fig.1.2, geological reservoirs, such as abandoned oil- or gas- reservoirs, are in fact soil formations, able to trap hydrocarbons and formation-fluids, forming so-called geological traps.



Figure 1.2: Examples of geological formations and their typical trapping

Soils are complex mixtures of minerals, water, air, organic matter, and countless organisms that are the decaying remains of once-living beings and this research desires to approach soils taking into account these complexity. In this research, the soil is not conceived as a continuum, but as an ensemble of discrete (or distinct) elements, or grains. By its definition, granular matter an agglomerate of macroscopic entities. Granular matter is always assumed to be athermal and deformable under stress.

In a geological reservoir filled with CO₂, the elementary units of granular materials can be meso- or micro-scopic grains which deform under two types of perturbation, namely chemical dissolution and lithostatic stress. The first one is due to the CO₂ that is injected in the reservoir, which can acidify the fluid already present in the geological formation, starting or enhancing their dissolution. Dissolving a grain, means that mass is loss from its original configuration and the mass loss can be acquired by the fluid. This can create instabilities inside the reservoir as the equilibrium prior to the CO₂ injection is loss. Now, it should be recalled that a reservoir adoptable for CO₂ storage needs a layer denominated porous media to host the CO₂ and a (preferably) integer layer with low-permeability denominated caprock, which seals the reservoir. When the in-situ dissolution takes place, it does not involve every part of the grain, but starts from the reactive mineral which characterized the target grain. If the porous media becomes target of a too excessive or too fast dissolution, there is space for the porous media to loose its initial configuration. At the same time, since the geological reservoir is a domain sited at a certain depth underground, every part of it is subject to a uniform and constant stress denominated lithostatic stress (or overburden pressure). This is the stress perceived by every geological layer, due to the above-standing soil.

To these days, a tool that can describe this situation for a geological reservoir is not available yet. In particular, there is need for developing a tool that can give more insights regarding the micro-scopic mechanical behavoior of a reservoir which undergoes chemical perturbation by means of dissolution, while the lithostatic load keeps acting on it. Two main difficulties should be overcome: the accessibility to the geological reservoir and the depiction of the grain deformation. As geological reservoirs are domains site at great depth (more than 800 meters underground), it can be inefficient and ineffective, therefore, expensive to approach the above-mentioned lack of knowledge by means of real sampling and drilling. Therefore, the research shifts toward numerical approaches which can be less accurate than experiments, but can give information more promptly, cheaply and can guarantee reusability of the tools. Secondly, while grains can have various 3D shapes, realistic modeling of the deformations of grains (or particles) is complicated. In this case, one can study deformations, by relating the interaction (or contact-) force to the overlap of two grains in contact.

This is one of the core feature of the discrete element method proposed by Cundall in 1979 [7], which is the selected numerical method. As the modeling of the realistic 3D shape of a grain and of its deformations is not always easy, some assumptions and idealizations are needed.

- 1. Grains are modeled as spherical, uniform and smooth particles
- 2. An homogeneous reservoir, made of spherical grains, is considered
- 3. A Representative element of volume (REV) of this domain is considered

4. The fluid is not explicitly modeled. Its chemical effect will be applied on each grains ¹.

With discrete element method simulations, the idealized REV is first prepared. Secondly, a real and typical lithostatic load (800 meters depth) is applied to the sample. Lastly, while the lithostatic load will remain active, chemical dissolution will be applied, which will be modeled as particle-radii reduction over time.

At any time of a DEM simulation, as the total force acting on a particle it is always known, it is then possible to obtain the magnitude of a contact force between two particles. This allows to compute bulk quantities that can be averaged over the volume of reference and obtain averaged stress situation in the specific volume. In addition, the sample, can be divided in smaller cells where quantities can be averaged. These can give more localized information throughout the simulation.

Relevant averaged bulk quantities.

- Stress tensor. In particular pressure and shear stress are analyzed.
- Coordination number
- Ratio between kinetic and potential energies

Relevant per-cell averaged quantities.

- Pressure
- Radius
- Volume fraction
- · Velocity

By managing these quantities in a DEM simulation, one can determine if the granular packing to which extent the granular packing which is modeled can be considered a solid or a fluid. If a transition from solid fluid can be observed while the same sample is being loaded, this will most likely mean loss of bearing capacity intended as collapse.

¹The dissolution of a particle is modeled as a particle shrinking in time. This means that particle radius will reduce over time. When applying this model, all the fluid effects are neglected

1.2 Thesis outline

The research conducted for M.Sc. Thesis is hereby outlined in Table 1.1:

	Thesis outline						
Chapter	Major information						
Chapter 1	Introduction and research questions						
	Introduction to the problem						
	Relevance of the research question						
	Research approach						
	Thesis outline						
Chapter 2	er 2 Theoretical background of CO ₂ geological storage						
	Knowledge essential to tackle the research						
	Mineral dissolution						
	Lithostatic load						
Chapter 3	Introduction to discrete element method						
	Introduction						
	Normal contact force						
	Tangential contact force						
	Cohesive contact force						
Chapter 4	Simulation Setup						
	Sample preparation						
	Phases of the simulation						
	Relevant quantities						
Chapter 5	Results						
	Results of the sample preparation						
	Results of the DEM simulations						
Chapter 7	Conclusion, Recommendations for future work						

Table 1.1: M.Sc. Thesis outline

Chapter 2

Theoretical background

In this section, the knowledge surrounding CO_2 geological storage which is essential to this research is presented. In Section 2.1, basic concepts of CO_2 geological storage are reviewed. In Section 2.1.1 the typical structure of a geological reservoir is depicted, followed by a review of the best practices in the injection of CO_2 . The following Section 2.1.2 reviews the basic storage mechanisms. This is needed in order to explain in which mechanism research falls into, which is a useful link into Section 2.2, where two major geochemical and geotechnical perturbations acting on any geological reservoirs are introduced. They are mineral dissolution and lithostatic load (also known as overburden pressure). Lastly, Section 2.3 highlights the importance of numerical simulations in this research. Subsequently the section will give more insights about which type of numerical simulations should be preferred, anticipating the introduction of the discrete element method.

2.1 CO₂ geological storage

Nowadays, CO_2 captured from the atmosphere is preferably injected into Geological formations, where storage can take place from decades or even centuries (Fig.2.1) [8] [1]. These formations, which are geologically referred to as "geological reservoirs", comprise several layers of transported and deposited (rock) grains, organic material, and minerals [9].

2.1.1 Geological Reservoir

The geological storage of the injected CO_2 , takes place in a geological reservoir. Such geological formation, depicted in Fig.2.2, comprises one layer of porous media, which will host the injected CO_2 in its pores, and a confining layer denominated caprock. The latter one is characterized by relatively low permeability, as its function is to seal the reservoir, prevent the CO_2 from reaching the Earth's surface.



Figure 2.1: Schematic representation of carbon capture and geological storage [10]





Best practices

The International Panel of Climate Change, also known as IPCC, has established some best practices [1], regarding how deep the injection should take place. The recommendation is to inject in formations at depth greater than 800 meters, as:

- CO₂ is likely to exist in its supercritical phase, which shows enhanced compressibility, compared to its liquid phase
- the high pressures encountered allow a decreased buoyancy difference (in comparison with the in-situ fluids), leading to an efficient pore filling

• in case of CO₂ leakage from the formation, decades are needed for the CO₂ to rise upto the Earth's surface. This can give time to decide upon mitigation options.

2.1.2 Trapping mechanisms

In addition, geological formations, ideal for storing CO₂, must show some structure-, materialand trapping mechanism- related, characteristics, which are hereby presented [1].

Structure-related. The formation must present a thick and extensive seal, also known as "cap rock", overlaying a porous media, that will store the injected- CO_2 in its pores (Fig.2.2) [1]. The cap-rock prevents the stored CO_2 from reaching the surface, while the porous media should be permeable enough to allows injection at relatively high flow rates without requiring overly high pressure [11].

Material-related. Ideal formations show high homogeneity and relatively similar grain distribution. Their pore structures varies with size, shape, and composition of the grains, and formation fluid (e.g. water or oil or gas) might be present in pores before CO_2 injection. As injected- CO_2 is stored in the pores, it can mix with such a fluid, creating new compounds.

Trapping mechanism-related. During geological storage of CO₂, three trapping mechanisms, are sequentially taking place.

- 1. *Structural trapping:* It is the physical storage of the CO₂ underneath the caprock, during the CO₂ injection
- Solubility trapping: It consists of the CO₂ dissolution into formation water. This process is desired as the CO₂ would no longer exist as a separate phase, eliminating buoyant forces. Within this step, formation-fluid acidity is likely to rise which can enhance mineral dissolution.
- 3. *Chemical trapping:* Lastly, the remaining-reactive CO₂ and formation minerals can react, creating new compounds. These reactions range from rapid (days), as for carbonate minerals, to slow, (hundreds to thousands of years) as for silica-based minerals.

2.2 Long-term storage under mineral dissolution

Among the lacks of knowledge within geological storage of CO₂, presented by the IPCC [1], the aim is to investigate to which extent the in-situ mineral dissolution affects the geotechnical stability of the reservoir, therefore its sealing capability. So far this has been studied only on a purely qualitative level [12] [6] and a tool able to compute the change in stress-strain due to mineral dissolution in a geological reservoir is not available yet. Therefore, basics of mineral dissolution and lithostatic load, which can be considered typical for storage conditions are hereby presented.

2.2.1 Dissolution

In chemistry, given a compound (solute) immersed in a fluid (solvent), the dissolution is defined as the transfer of mass from a solute into a solution, by means of a solvent. In the present work, only solid solutes are considered [13]. As depicted in Fig.2.3, when the compound is immersed in a solution, it can first break down into smaller pieces before dissolving [Fig.2.3].



Figure 2.3: Schematic representation of the dissolution: (A) the initial compound, (B) the compound immersed into solution, and (C) the compound dissociation into solution. [13]

Three main factors can increase dissolution, namely:

- · An increased reactive surface area offered by the solute
- An increase in temperature in the system
- · Enanched chemical affinities between elements in solution

Dissolution and bearing capacity

From a more (geo)structural perspective, a solid compound exibits a capability of bearing loads, if applied on it [14]. This is commonly referred to as bearing capacity. When the compound gets dissolved, its solidity decreases as less structure is contributing in bearing those loads.

In CO_2 geological storage, the porous layer is the main target of dissolution as it can host a mix of formation fluids, hydrocarbures and CO_2 [15] [1], which will be likely present in its supercritical phase.

Mineral dissolution can first cause variations in the porosity and permeability of the medium. As grains change in size and mass is transferred to the formation fluid, instability can then occur, which can destabilize the caprock and arming the sealing capability of the reservoir.



Figure 2.4: Schematic representation of the lithostatic load [22]

Mineral dissolution and supercritical CO₂. When stored in the porous media of a geological reservoir, the CO₂ is most likely present in its supercritical physical state, due to high pressure and temperature in the geological formation [16] [6]. Storing CO₂ in its supercritical phases is highly desired, as it shows enhanced compressibility, lowered toxicity and it is not flammable [17]. Nevertheless, supercritical CO₂ is a well-known solvent [17], which can enhance dissolution by means of acidification of water [18] [19] [20].

Lithostatic load. Since the porous media of a geological reservoir, is a geological domain sited at a certain depth underground (2.4), while being subject to dissolution, stress comining from the weight of overlying soil is also present. [21] [22].

This is called lithostatic stress and it is referred to as σ_v (The reader should be aware that in many books σ_v indicates the deviatoric stress). This is a depth-dependent constant stress imposed on a soil layer. It can be calculated as from Eq. 2.1:

$$\sigma_v = \rho \cdot g \cdot z = \gamma_s z + q \tag{2.1}$$

where the litostatic load, σ_v has the unit of a pressure [N/m² = Pa] and can be seen as a uniform load at each depth, ρ is the density of the overlying soil [kg/m³], g is the gravitational acceleration (9.81 m/s²) and z is the depth in meters. In a more concise formulation, it can be calculated as function of the specific soil weight (γ_s), the depth and the surface surcharge q proper of the crust [22].

2.3 Numerical simulation in CO₂ geological storage

From the design to the monitoring of a geological reservoir, information needs to be sampled as promptly, cheaply and constantly as possible. Nevertheless, geological reservoirs are located at depths where accessibility to in-situ information not always easy. Numerical simulations can to cope with this issue. They are computational tools allowing to model (parts of a) geological reservoir on a computer, assigning physical properties, which can be gathered from previous experience, literature or laboratory experiments [23] [24]. One can then apply a (combination of) thermal, chemical or mechanical perturbation to the virtual element and observe its response over a certain time [25].

Drivers for using numerical simulations. Nowadays, soil engineering related companies and academics are increasingly driven to use numerical simulations within CO_2 geological storage.

First, computers with high processing capabilities are constantly decreasing in price, as present-day computer graphics allows to visualize the outlook of the reservoir. Visualizing the simulations can be of added value when negotiating with stakeholders and can increase public outreach by means of demonstrating videos.

Secondly, numerical simulations allows to analyze different reservoirs re-using previous codes. This is less time and money consuming than real sampling or seismography.

In general, computer simulations work with the numerical solution of governing equations. In many circumstances they may prove to be the only possible means to address the principal public and environmental concern related to the long-term fate of the carbon storage.

Discrete element method vs Finite element method

Among currently available numerical simulations, two mainstream options - the discrete element method (DEM) and the finite element method (FEM) are among the most used methodology to simulate geomechanical problems. Their difference can be visualized in Fig.2.5. In DEM, the medium is conceived as a series of polygonal rigid blocks, each one free to move in 3D. The deformation of the medium and magnitude of the force between blocks both depend on the overlapping volume and amount of slip between blocks. DEM allows to observe the micromechanics of the problem, for example, it can be widely adopted for studying grain crushing. Unlike in FEM simulations, DEM allows a grain level control. In addition, DEM makes large displacements between elements easy to simulate and surpasses FEM when dealing with discontinuous problems, which is a case where FEM becomes computationally demanding. The main advantage of using DEM is that the method can be used to solve problems on movement of blocky systems, with large scale discontinuous displacements, such as translational or rotational motion of blocks or a single block. DEM, is therefore, more suitable for simulating problems which involve discontinuous deformation and failure of blocky media [26].

On the other hand, FEM treats the material as a continuum matter. It assumes that a continuum can be divided in smaller areas, then reconnects elements at "nodes". One can see nodes as pins or drops of glue that hold elements together. This process results in a set of simultaneous algebraic equations. Many engineering phenomena can be expressed by "governing equations" and "boundary conditions". It is very difficult to make the algebraic equations for the entire domain. Divide the domain into a number of small, simple elements.



Figure 2.5: Comparison between FEM (left) [?] and DEM (right) [27] applied to slope-related problems

A field quantity is interpolated by a polynomial over an element. Adjacent elements share the DOF at connecting nodes. Obtain the algebraic equations for each element A general closed-form solution, which would permit one to examine system response to changes in various parameters, is not produced. The FEM obtains only "approximate" solutions [28] [29].

The present research adopts the discrete element method as numerical method. In first place, the nature of the collapse in soils is prevalently of discrete nature, dominated by the low-scale kinematics. If one would like to adopt FEM for this research, one should bear in mind that, a constitutive law needs to be applied to each node. Each node of the FEM approach is the equivalent of a set of agglomerates and a unique constitutive law for such a configuration has not been found yet. Therefore, by using FEM, the first risk is to miss realistic information, especially regarding the collapse of the sample. Therefore, instead of trying to define a constitutive law (where the stress σ would be function of the Young's Modulus referred to the bulk, which is not a microscopic quantity), which is likely to be extremely inaccurate and unrealistic, one could describe the stress σ by means of a contact law, which is an accurate description of the contact between two grains. This approach

is peculiar of DEM. For example if one would decide to adopt the Hertzian contact law, high accuracy in the description of the grain-grain contact is achieved. In addition once the contact force between two grains is known, one can compute the stress, but without making use of a constitutive law.

Lastly, the present research deals with sets of granulates which can change, even instantaneously, their size due to their chemical dissolution. In DEM, this can naturally happen without extra computational power nor artifacts, since each body is independent and free to move in 3D. If one would use FEM, one should divide the continuum, which in our case is a sample of soil, into smaller areas, which are tight to each other by the nodes. At this point, if one would like to implement the possibility for each area to move, nodes would need to be removed, which is a relatively computationally expensive stage.

Chapter 3

Numerical Methodology

As anticipated by the last section of the previous chapter, the discrete element method has been preferred over finite element method for conducting this research. Therefore, DEM is the selected numerical methodology which will be introduced in the present chapter. In particular, the concepts reviewed in this chapter, will be the base of the simulation setup depicted in the following chapter (see Chapter 4).

First, in Section 3.1 the reader can find an overview of the basic concepts of the discrete element method. Since the understanding of DEM is link to either the knowledge of the equations of motion or the calculation of forces acting on particles, the following part of this chapter first reviews the equations of motions and then reviews contact forces, divide in normal and tangential. In particular, the basics of the non-linear contact model (or Hertzian contact model), are first reviewed, followed by the basics of the normal cohesive forces which needs to be added to the classical Hertzian model. A review the basics of the tangential contact forces follows. Subsequently, Section 3.1.3 reviews numerical aspects intrinsic in DEM. Therefore, the concept of time integration is first reviewed. Setion 3.1.4 reviews macroscopic quantities of interest in DEM simulation that can be obtained by averaging contact information. Lastly, Section 3.1.5, will explain the rationale behind the choice of LIGGGHTS (in its version v.3.3.1), as software.

3.1 Introduction to discrete element method

The discrete element method (DEM), first proposed by Cundall and Strack in 1979 [7], is a numerical algorithm which is often used for describing how granular material behave [30]. This method is closely related to molecular dynamics (MD), and it is mostly used to simulate the motion of macroscopic particles [23]. Being based on Newton's equation of motion, the goal of DEM-simulation is to describe the time-dependent positions and velocities of each particle in a particle assembly.

In DEM, two main calculation cycles are conducted, as depicted in Fig.3.1.

First the motion of the particle is calculated by means of time-integration. The dynamics of a system of particles is modeled by tracking the motion of individual particles and their



Figure 3.1: Calculation cycle in DEM (source: the Author).

interaction with their adjacencies over time [31]. Subsequently, if two particles are in contact (as in Fig.3.2), an overlap between the particles can be generated and a force deriving from the contact is calculated. The entity of this force depends on the force-displacement law. This is also known as the contact force. In a DEM-algorithm once the forces acting on one particle are known, one can integrate the equations of motion to get the new positions and velocities per particle for the next time-step [7] [23] in a cyclical manner.

Alongside external forces on the particles, the contact forces, play an important role in the force calculation procedure. Typically, particle contacts are firstly searched at each time-step of a simulation, secondly their contact forces are determined, accordingly.

3.1.1 Equation of motion

If all forces f_i acting on the particle *i*, either from other particles, from boundaries or from external forces, are known, the problem is reduced to the integration of Newton's equations of motion for the translational and rotational degrees of freedom [23]:

$$m_i \frac{d^2 u}{dt^2} r_i = f_i + m_i g \tag{3.1}$$

and

$$I_i \frac{d}{dt} \omega_i = t_i \tag{3.2}$$

with the mass m_i of particle *i*, its position r_i the total force $f = \sum_c f_c^i$ acting on it due to contacts with other particles or with the walls, the acceleration due to volume forces like gravity g, the spherical particles moment of inertia I_i , its angular velocity ω_i and the total torque $t_i = \sum_c (l_i^c \times f_i^c \times q_i^c)$, where q_i^c are torques/couples at contacts other than due to a tangential force, e.g. due to rolling and torsion [23].



Figure 3.2: Schematic representation of discrete element method [23]

3.1.2 Contact forces

Normal contact force

Analyzing the normal component of the contact force, two contributions are present, namely elastic and viscous. The normal contact force can then be written as sum of these two contributions, as:

$$f_c^n = f_{elastic}^n + f_{viscous}^n \tag{3.3}$$

The presence of the elastic deformation implies that after separation from contact, particles can recover their initial shape [23]. Contact between two continuous, non-conforming solids is initially a point or line. Under the action of a load the solids deform and a contact area is formed [32]. Hertz contact stress theory allows for the prediction of the resulting contact area, contact pressure, compression of the bodies, and the induced stress in the bodies [33]. This is a non-linear contact model, in which the normal force is based on the Hertzian contact theory and gives a nonlinear elastic relationship between normal contact force and displacement [33]. For sake of completeness, an alternative to the Hertzian contact model is the linear, or hookean, contact model. Nevertheless, the Hertzian contact model represents the most accurate definition of the normal contact force borne from two particles in contact [34]. **Non-Linear normal contact model** In general, two colliding spheres undergo a deformation which will be somewhere between the extremes of perfectly elastic and perfectly inelastic [34] [23]. Possible mechanisms for dissipations (which include, transformation of kinetic energy into other forms of energy which ultimately transform into heat) are plastic deformation, viscoelasticity of the material, and also elastic waves excited by the impact. The latter are always present. Phenomenologically, the elasticity of the impact is described by the coefficient of normal restitution e_n , as from:

$$e_n = -\frac{v_n^f}{v_n^i} \tag{3.4}$$

where v_n^f and v_n^i , respectively, are the collision right after and before the collision. Modeling a force that leads to an inelastic collision requires at least two terms to be known, namely the repulsive term and the dissipating term. A very accurate manner to calculate this force, can be done by means of the Hertzian theory of elasticity, which predicts the following repulsive force for the case of spherical particles.

$$f_c^n = -\tilde{k_n}\delta_n^{\frac{3}{2}} \tag{3.5}$$

Here, $\vec{k_n}$ is a non-linear stiffness connected to the elastic properties and to the radii of the spheres through $\tilde{k_n} = 4/3 \sqrt{r_{Eff}} E_{Eff}$, with r_{Eff} being the effective radius and E_{eff} the effective Young's modulus, between two particle. Effective means that quantities, is expressed in relation to two (or more) particles which can be in contact. When only one particle type is used, the effective quantity is equal to the quantity of that specific material specie. Within this research the following effective quantities are of interest. Namely, they are the effective radius (Eq.3.6), mass (Eq.3.7), Young's Modulus (Eq.3.8) and shear modulus (Eq.3.9).

$$r_{Eff} = \frac{r_1 + r_2}{r_1 r_2} \tag{3.6}$$

$$m_{Eff} = \frac{m_1 + m_2}{m_1 m_2} \tag{3.7}$$

$$E_{Eff} = \frac{E_1 E_2}{E_2 (1 - \nu_1^2) + E_1 (1 + \nu_2^2)}$$
(3.8)

$$G_{Eff} = \frac{E_1 E_2}{2E_2 (2 - \nu_1)(1 + \nu_1) + 2E_1 (2 - \nu_2)(1 + \nu_2)}$$
(3.9)

As the original Hertzian formulation does not include viscosity, but only repulsive forces betwen two spherical particles in contact, a dissipative a viscous damping term is added obtaining a damped Hertzian contact model.

$$f_c^n = -\tilde{k_n}\delta_n^{\frac{3}{2}} - \gamma_n \dot{\delta_n}$$
(3.10)

where the viscous term includes the damping coefficient, γ_n and it is function of the velocity, which can be written as derivative of the overlap, $\dot{\delta_n}$. Alternatively viscosity, can

be expressed as function of the restitution coefficient e_n , calculating the so-called damping constant β_d :

$$\beta_d = \frac{ln(e_n)}{\sqrt{((ln^2(e_n)) + (\pi^2))}}$$
(3.11)

Cohesive contact model In the original formulation of the Hertzian contact, cohesion between particles is not taken into account. This contribution can be taken into account by adding a cohesive contact model [35]. If one would neglect the long-range cohesive forces, assuming that only short-range forces are present, the simplest model is for including cohesion between particles is a simplified version [36] of the model presented by Johnson, Kendall and Roberts, also known as JKR model [37]. In this model, two particles in contact only feel attractive force across the contact region while the surface areas outside the actual contact area are force free. This version of the JKR model provides an expression for Van der Waals force calculation:

$$f_{JKR} = c.e.d(2\pi\delta_n 2r_i^2) \tag{3.12}$$

where c.e.d. is the cohesive energy density which expresses the amount of energy needed to completely remove unit volume of molecules from their neighbors to infinite separation. It is generally measured in J/m³. The cohesive force f_{JKR} is also function of the overlap (δ_n) and radius (r). JKR is in fact an approximation to the general solution which must account for both the surface forces acting on outside the contact area and the principles of contact mechanics controlling the deformations within the contact area. For a more detailed comparison between cohesive contact models the reader can consult the following reference [37].

Tangential contact force

In a collision, together with a normal contact force, a tangential contact force can be generated. The contact tangential force, f_c^t is given by the sum of tangential spring force, f_c^{ts} , and tangential damping force, f_c^{td} , as given by:

$$f_c^t = (f_c^{ts} + f_c^{td})$$
(3.13)

The tangential spring force is expressed in incremental terms, as:

$$f_c^{ts} = (f_{c,(n-1)}^{ts}) + \Delta f_c^{ts}$$
(3.14)

where, $f_{c,(n-1)}^{ts}$ is the tangential spring force at the previous time-step, and Δf_c^{ts} ts is the increment of tangential force which is given by:

$$\Delta f_c^{ts} = -k_t \Delta t \tag{3.15}$$

where Δt is the time-increment between two consecutive time iterations, k_t is the tangential stiffness, and is the increment of the tangential displacement. It can be calculated as:

$$k_t = 8G_{Eff}\sqrt{r_{Eff}\delta_n} \tag{3.16}$$

Where G_{Eff} and r_{Eff} are the effective shear modulus and radii, respectively. The damping force is given by the following relationship:

$$f^{td} = 0.745\beta_d \sqrt{m_{Eff} k_t} v_{rel,n} \tag{3.17}$$

with $v_{rel,n}$ being the relative normal velocity between two particles. Lastly, a truncation could be applied to the tangential contact force, using the Coulombic friction criterion:

$$f_c^{ts} \le \mu f_c^n \tag{3.18}$$

with μ being the coefficient of static friction. In this procedure, the tangential contact force is always specified to be lower than the normal contact force.

3.1.3 Numerical specific aspects

Time integration

.

The concept of discretization in numerical mathematics explaining the transition from a problem that is posed on a continues interval to a problem that is only posed at a finite number of points. Discretization is used in the solution of differential equations to transform the differential equations into a system of equations with an approximate solution only at the chosen point. One of the most efficient and stable approaches for the time discretization of Newton's equations is the Verlet-algorithm. Many softwares make use of a variants of Verlet-algorithm called Velocity-Verlet-algorithm. In this method, the position and velocity update at the same time value of the time variable.

$$\overrightarrow{x}(t+\Delta t) = \overrightarrow{x}(t) + \overrightarrow{v}\Delta t + \frac{1}{2}\overrightarrow{a}(t)\Delta t + O(\Delta t^4)$$
(3.19)

$$\overrightarrow{v}(t+\Delta t) = \overrightarrow{v}(t) + \frac{1}{2} [\overrightarrow{a}(t) + \overrightarrow{a}(t+\Delta t)] \Delta t + O(\Delta t^2)$$
(3.20)

where Δt is the time step and \vec{a} is the acceleration owned by the particle. The local errors for position and velocity are $O(\Delta t^4)$ and $O(\Delta t^2)$. However, the global error is of the order of $O(\Delta t^4)$ for both velocity and position. The implementation scheme fo this algorithm is as follows:

1. The first step is to calculate:

$$\overrightarrow{v}(t + \frac{\Delta t}{2}) = \overrightarrow{v}(t) + \frac{1}{2}\overrightarrow{a}(t)\Delta t$$
(3.21)

2. The second step is to calculate:

$$\overrightarrow{x}(t + \frac{\Delta t}{2}) = \overrightarrow{x}(t) + \frac{1}{2}\overrightarrow{a}(t)\Delta t$$
(3.22)

3. The third step is to derive from the interaction:

$$\overrightarrow{a}(t+\Delta t) \tag{3.23}$$

4. Fourth, one needs to calculate:

$$\overrightarrow{v}(t+\Delta t) = \overrightarrow{v}(t+\frac{\Delta t}{2}) + \frac{1}{2}\overrightarrow{a}(t+\Delta t)\Delta t$$
(3.24)

Time-step. DEM simulation also require to define a proper time-increment, also known as time-step between two consecutive iterations. A sufficiently small integration time step is required in order to obtain stability of the simulation by means of having a sufficient number of time steps within each collision. In a granular system assembly, force transmission between individual particles is through the Rayleigh wave ¹ that travels around the surface of elastic bodies. The DEM time step should be chosen such that the time step for calculating particle information should be less than the time required for a Rayleigh wave to transverse the minimum size particle in the assembly. In general, best practices suggest that the time-increment could be 1/40, 1/50 or 1/100 of the shortest contact time. The collision time t_c is dependent on the impact velocity and can be calculated as:

$$t_c = 3.21 \left(\frac{m_{eff}}{\tilde{k_n}}\right)^{\frac{2}{5}} (v_n^i)^{-\frac{1}{5}}$$
(3.25)

At this point, the choice of the numerical time-step Δt must depend on the maximum relative velocities expected during the simulation to ensure satisfactory numerical accuracy.

3.1.4 Relevant averaged output quantities

The macroscopic behavior of granular materials can be understood from the microscopic analysis of their constituents interacting through contact forces. In this section, definitions of averaged quantities used in the research is presented. From the microscopic quantities, it is possible to obtain averaged output which can give information regarding bulk characteristics. Furthermore, by dividing a simulation domain into smaller cells, it is possible to average quantities, obtaining per-cell averaged quantities. These can give more localized information regarding the bulk behavior.

¹Rayleigh waves are a type of surface acoustic wave that travel on solids. They can be produced in materials in many ways, such as by a localized impact or by piezo-electric transduction, and are frequently used in non-destructive testing for detecting defects. They are part of the seismic waves that are produced on the Earth by earthquakes.

Averaged-stress tensor. From the simulations, one can determine the stress tensor (compressive stress is positive as convention) components, as from the following equation:

$$\sigma_{ij} = \frac{1}{V} (\sum_{V} m^{p} v_{i}^{p} v_{j}^{p} - \sum_{V} f_{i}^{c} l_{j}^{c})$$
(3.26)

with particle p, mass m_p , velocity v_p , contact c, force f^c and branch vector l^c . The first sum is the kinetic energy density tensor while the second involves the contact-force dyadic product with the branch vector. Since the present setup deals with quasi-static condition, the first sum of Eq.3.26 can be neglected. In such a case, stress in a granular medium can be seen is the volume average of dyadic products of branch vectors l^c and contact forces f_i^c among all contacts within an assembly:

$$\sigma_{ij} = \frac{1}{V} \sum_{1}^{N_p} f_i^c \otimes l_j^c$$
(3.27)

In granular media, the isotropic stress is denoted as hydrostatic pressure:

$$p = \sigma_v = \frac{1}{3} tr(\sigma) \tag{3.28}$$

Deviatoric stress. The deviatoric stress, σ_v , can be calculated as:

$$\sigma_v = \sqrt{\frac{1}{2}((\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2) + 6(\sigma_{12}^2 + \sigma_{23}^2 \sigma_{32}^2))}$$
(3.29)

but in case of uniaxial compression, a simplified version can be used, which is Eq.3.30

$$\sigma_v = \sqrt{\frac{1}{2}((\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2))}$$
(3.30)

Coordination number. The average coordination number can be defined as:

$$C = \frac{2N_c}{N_p} \tag{3.31}$$

where N_c is the number of contacts and N_p is the number of particles considered.

Kinetic and Potential energy ratio. The kinetic energy of a granular packing is the summation of all kinetic energies owned by each particle. This can be expressed as:

$$E_{Kin} = \sum_{i=1}^{N_p} \frac{1}{2} m_i v_i$$
(3.32)

where N_p is the number of particles in the system, m_i and v_i are respectively, mass and velocity of the ith particles. The potential energy, derived from the Hertzian contact model can be expressed as:
$$E_{Pot,Hertzian} = \sum_{i=1}^{N_p} \frac{8}{15} E r^{\frac{1}{2}} \delta_n^{2.5}$$
(3.33)

Furthermore, it is possible to divide a DEM simulation domain in smaller cell, where output quantities can be averaged. This can return more localized information regarding the bulk behavior. In the present research, the following quantities are included in per-cell averaging: pressure, velocity, radius and volume fraction. The pressure can be calculated as in Eq.3.28. The velocity and the radius are calculated as for the entire domain, but in a reduced domain. Similarly as for the radius, the volume fraction can be calculated as from its definition with spherical particles:

$$\phi = \frac{N_{grains} \frac{4}{3} \pi r_i^3}{V_{cell}} \tag{3.34}$$

where, N_{grains} is the number of grains calculated in the cell, r is the averaged radius and V_{cell} is the volume of the cell.

3.1.5 Software

For simulations, LIGGGHTS which is an open source software for particle simulation with discrete element method [38]. LIGGGHTS has several advantages for our aims. The important ones for this research are:

- · It is available as freeware
- · It offers the possibility of exporting simulation results in video format
- It offers the possibility of creating a simulation box of any shape, with the option of creating multiple layers inside the same box
- · Tutorials are included when downloaded
- Assistance by means of forum is relatively quick in answering questions (circa 1-day latency)

LIGGGHTS is an Open Source Discrete Element Method Particle Simulation Software [39]. The name LIGGGHTS stands for LAMMPS improved for general granular and granular heat transfer simulations. LAMMPS is a classical molecular dynamics simulator which provides the basic codes for LIGGGHTS. It is widely used in the field of Granular Dynamics.

Chapter 4

Simulation Setup

In the present chapter, the methodology established to conduct the DEM simulations within the present work, is presented. Since the modeling of a domain requires the transition from a physical domain to modeled domain, Section 4.1 initially explains under which assumption this step is conducted. This section aims to explain how each of the physical phases of the reservoir, are modeled within this setup.

In Section 4.1.1 the concept of the representative element of volume is adopted as it could help studying the bulk characteristics by means of one volume, instead of studying one the whole domain. In order to create a numerical REV, more phases are needed. In the last part of this section, the reader can find first how these phases are conceived. In addition, each of these phases can be staged by means of the quantities introduced in the previous chapter.

Section 4.1.2 explains the details of the sample preparation. The section depicts which and how material input parameters are selected, how the domain is constructed, explains how the REV is generated within DEM, highlight how the volume fraction has been selected, define typical characteristic of each simulation phase and introduce the time-step adopted for the simulations. Subsequently, it is explained how the lithostatic load is conceived assuming that the load is applied by discrete elements.

Section 4.2 depicts the experimental formulation of the mineral dissolution, is firstly introduced. In a transition from real experiments to DEM simulations, it is possible first possible to gather initial and final mineral mass, before and after dissolution, at saturation. Further on, a negative exponential trend for mass reduction during dissolution, can be assigned to real experiments. The mineral dissolution typical for a geological reservoir, can be modeled as a set of particles that are shrinking in radius over time. Two modes are introduce, depending on if one would like to include a threshold defined by the fluid saturation (limited shrinking), or if this is neglected (unlimited shrinking). In both cases, a transition from experiments is possible, under this assumption of constant density and particle mass loss equal to a loss in radii. Initial and final mass, therefore, radii of a particle undergoing dissolution, can be collected from experiments. Since it is of interest to understand how often the dissolution occurs, a turnover frequency can be calculated experimentally and numerically. The latter one is adopted to cope with the shorter amount of time in DEM simulation, compared to the real experiments.

4.1 Modeling simplifications

With numerical simulations it is possible to recreate in few seconds a set of granulates that nature has built in millenia [40] and then extrapolate averaged quantities which can reproduce the bulk behavior. Nevertheless, a modeling consists of transferring physical characteristics of the reservoir to a model. One firstly need ot define the assumptions that can simplify the physics and the characterization of the geological reservoir. Subsequently information can be grasped by analyzing a sample which is representative of a simplified macroscopic domain [41] [42]. This step can be visualized in Fig.4.1



Figure 4.1: Selection of the domain of interest (left picture, [10]), followed by the a concept design of the particle simulation of the selected domain (right picture, source: the Author)

4.1.1 Assumptions

Before starting the DEM modeling, the following geological reservoir-related simplifications are assumed present research:

 System-related. It is assumed that temperature is a constant. It is then assumed that only chemical effects and the lithostatic load are perturbing the grains. Therefore, it is assumed that only lithostatic load and dissolution are affecting the sample. The lithostatic load is considered constant over time, while the dissolution is assumed to target every grain. It is assumed that the lithostatic load acting on the reservoir is equal to 10⁷ Pa, which is a most likely value according to the best-practices by IPCC [1]. Using on of the IPCC nomenclatures, it is assumed that the geological belongs to the monitoring phase of the reservoir [1].

- 2. Fluid-related. It is assumed that the geological reservoir of interest, is in a storage phase considerable far from the injection. It is assumed that the no hydrocarbon is present in the reservoir but only formation water, which is CO₂ saturated but is still able to react with the surrounding grains. The mixing between the fluid contained in the formation and the supercritical CO₂ can be considered as slow, but possible and the velocity of the fluid can be considered very small. The effect of eventual in-situ bacteria is neglected. It is assumed that the fluid can react much faster than it can diffuse within pores. Therefore, the diffusivity of the fluid of interest is an idealized mixture of formation water and supercritical CO₂. This research aims to gather insights during the immediate activation of a dissolution process. The interest is to understand what happens in the immediate time-frame after grains might start dissolving due to supercritical CO₂ driven acidification. The chemical effects of the fluid mixture on the grains is known, and it is assumed that this effect can be modeled instead of explicitly representing the fluid itself.
- 3. Material-related. It is assumed that the grains characterizing the geological reservoir, can be modeled as spherical and smooth particles. It is also assumed that all pores are completely filled with a mixture of formation fluid plus CO₂. The sample of interest should be representative of an interface between caprock and porous media, as major problems are localized in this part of the geological reservoir. For sake of simplicity each grain is assumed to be a spherical and homogeneous particle. Regarding the mineralogy of the reservoir, geological reservoirs are likely to be silica- and carbonate-rich, since these minerals are the most recurrent in the Earth's crust. In addition to the assumption of spherical homogeneous particles, it is assumed that each grains is homogeneously made of either silicate or carbonate.

Numerical preparation

Once the assumptions regarding the geological reservoir are defined, one can study a representative elementary volume (REV) instead of the whole domain. A REV (also called the representative volume element (RVE) or the unit cell) is the smallest volume over which a measurement can be made that will yield a value representative of the whole [43]. For a sample of a heterogeneous material to be a REV, it should be entirely typical of the whole mixture on average and contains a sufficient number of inclusions for the apparent properties to be independent of the surface values of traction and displacement, so long as these values are macroscopically uniform [43]. Nevertheless, in numerical simulations, it is unlikely that one could recreate a sample and apply a perturbation making by means of one simulation phase only. For numerical reasons, there is need for distinct phases, in which the REV can be first prepared and then subjected to the dissolution, in our case. In more details,

the present research defines the following simulation phases, which can be stage by means of quantities discussed in Section 3.1.4 which can be visualized in Fig.4.2 and summarized in Table 4.2:

- Initially, particles need to be numerically created. Therefore, following input are needed, namely, radius, particle density and the initial volume fractions of the system. In this phase one can also define the boundary conditions of the simulation, which can be fixed (real walls are inserted), periodic (particles are free to re-enter the simulation domain if there is collision with simulation boundary) or a combination of the above. By means an iterative approach, the optimal duration of this phase is found to be 1000 time-steps long.
- 2. When particles are inserted, they have some overlap, which can generate repulsion between particles and therefore, high kinetics in each region of the simulation. This situation is not likely to return two stable regions and it likely to enhance the mixing of the two particle types. Therefore, these kinetics need to be lowered as much as possible, by means of relaxing each particle type in its correspondent region where it has been inserted. When the ratio between the kinetic and potential energy averaged over each region, can be considered stably low (lower than 10⁻⁶, as suggested by best practices),the separator-wall between the two regions can be removed, letting the two bulks to lay on top of each other. The bulks will be able to coexist in the same simulation as stable solid compounds, with negligible mixing. By means an iterative approach, the optimal duration of this phase is found to be 3000000 time-steps long.
- 3. When the removes the separator-wall, some new kinetics is still applied to the system, since the empty gap initially occupied by the separator-wall can now be filled with particles. Therefore, a new relaxation is needed in the simulation. This phase is again conducted until the packing can be considered stably low (lower than 10⁻⁶, as suggested by best practices). By means an iterative approach, the optimal duration of this phase is found to be 3000000 time-steps long.
- 4. Subsequently, the lithostatic load is applied to model the process of compaction and sedimentation that the sample has undergone over time in a soil. The lithostatic load is generally conceived as constant load, which can act with same intensity at same depth. Due to the discreteness of the grains in a soil, from this load, a force acting on grains is calculated. Therefore, the lithostatic load is modeled by means of a force acting in the same direction as the load. This phase should generate a stable sample, in which the averaged stress is lower then the target lithostatic load. For sake of simplicity this is modeled as an instantaneously applied force which can remains constant for the remaining simulation time. By means an iterative approach, the optimal duration of this phase is found to be 3000000 time-steps long.
- 5. At this point, the sample is ready to be subjected to either the lithostatic load or the chemical dissolution. Therefore, in a following phase all particles representing grains

of the porous media are meant to be target of dissolution. This phenomenon is represented as a set of particles shrinking in size. By means an iterative approach, the optimal duration of this phase is found to be 10000000 time-steps long.



Figure 4.2: DEM operative schema

As also notable in Fig.4.2, quantities are averaged in a two-folded manner. Bulk quantities are averaged in each region of the porous media and caprock respectively) On the other hand one can calculate per-cell averaged quantities, computed in cells of cubic shape calculated as multiple of a maximum cutoff which is input in LIGGGHTS. The dimension of each cell is left up to the internal algorithm of the software. The minimum value possible is the input of this cutoff, therefore setup deals with 27 cells. Now, some of these cells are more relevant, namely the so-called "central" cells. In the research Central cells are three cells which belong to the central column with respect to the total sample. For simplicity, these region are named with number as they are output by LIGGGHTS and they are: Region 5 is the lowest central region, Region 14 is the middle and Region 23 is the highest. The per-cell averaged setup can be visualized in Fig.4.3

4.1.2 Sample preparation

In the following Table 4.1, the selected input parameters for preparing the REV are collected. The column collecting input for the caprock is unique. On the other hand the porous media is modeled a variable mixture of two possible materials, namely silicates and carbonates. Therefore, a variable mixture of both materials in inserted in the porous media.

Material properties. The sample is made of two regions. The upper region, represents particles in the cap rock while the lower one represents the porous media. Caprock particles are modeled as a set of spherical cohesive particles, with Young's Modulus equal to



Figure 4.3: Points of averaging for each cell. In the figure, the centers are presented. Each cell is a cubical domain of 0.3 m per side.

10¹¹ Pascal and a Poisson ratio equal to 0.35. The relatively high cohesion is a manner to model high permeability on a microscopic level and this configuration is meant to represent a highly compressed sandstone with traces of iron, which is considered representative of high stiffness.

To model the mixed composition of the porous media region, which is the lower part, corresponding particles are placed according to a variable mixture in weight of silica and carbonates. Five different mixtures are designed. Two of them represent mixtures that comprise only silica and carbonate respectively, while the other three represent a combination of 25% - 75%, 50% - 50% and 75% - 25% in weight, respectively. These particles are modeled with two Young's Modulus, namely 10¹⁰ for silicates and 10⁹ for carbonates, while the Poisson ratio equal to 0.35. For the characterization of both regions, data are taken from the literature. All types of particles have a coefficient of static friction equal to 0.35 and a coefficient of restitution equal to 0.8. Typical material property for DEM simulations are define.

The particle density, (not the bulk density, which is a macroscopic quantity), should be first defined together with the initial volume fraction and particle radius, since the research deals with spherical particles. It is general practice to set this value equal to the standard density of solids which is 2700 kg/m³. Such a standard value is inserted for both regions.

Particle radii. When choosing the particle radius, one can define a monodisperse packing, which is a packing with particles all of the same sizes, or a polydispersed packing, where particle can have different sizes. A very common manner to operate, is to define a central (or

Input	Caprock	Carbonates	Silicates				
E	10 ¹¹ Pa	10 ⁰⁹ Pa	10 ¹⁰ Pa				
ν	0.35	0.35	0.35				
е	0.8	0.8	0.35				
μ	0.35	0.35	0.35				
C.e.d.	2000 Pa	0 Pa	0 Pa				
Poly-dispersity	1.2	1.2	1.2				
Radius	0.015 - 0.018 m	0.02 - 0.023 m	0.02 - 0.023 m				
Volume fraction	0.62	0.62	0.62				
Particle density	2700 kg/m ³	2700 kg/m ³	2700 kg/m ³				
Particle shape	spherical	spherical	spherical				

REV characteristics

 Table 4.1: Characteristics aimed for the REV of this research

average) value of a certain radius and then define a certain distribution (typically Gaussian or normal). This can allow the generation of packing with particle radii ranging from a r_{min} to a r_{max} and this procedure is typically conducted to avoid crystallization.

Therefore, in both regions, particle radii are designed with a uniform distribution in radii, creating a slight polydispersity, to avoid the crystallization. The radii ranges in the following fashion: the cap rock particles have a minimum radii of 0.015 meters and a maximum equal to 0.018, while for silicates this ranges from 0.02 to 0.023 and carbonates from 0.025 to 0.028 meters.

Volume fraction. The volume fraction represent the porosity of the packing and it is formulated as:

$$\phi = \frac{V_{solid}}{V_{total}} \tag{4.1}$$

where V_{solid} is the total volume occupied by the spheres, the solid part, while V_{total} is the total volume of reference (of the REV in this case). It should be remembered that the volume fraction and the porosity are two different manner to express soil porosity. Now it is desired to insert particles in their correspondent region, with an initial volume fraction equal to 0.62, for each layer. When designing the sample, the volume fraction can help checking if the sample volume is correctly matching a proper number of (spherical) element. Assuming that one should have at least 4000 particles, with an average radius equal to 0.02 meters, and a volume fraction equal to 0.62, one can calculate:

$$0.62 = \frac{4000\frac{4}{3}\pi r_i^3}{V_{Total}}$$
(4.2)

one can obtain a total volume equal to 0.216 m³. In cubical domains, this is equal to a

cube with each side equal to 0.6 meters. Another check is regarding the internal stress situation after relaxation. A representative volume fraction should return a sample that, in stable condition, exhibit a stress condition lower than 10⁷ Pa. It is hereby reminded that such a load can represent the most likely value in a geological reservoir. Secondly, after relaxation the internal stress of such a packing is lower than . This check has been conducted iteratively, starting from 0.7 and decreasing by 0.1 each time. The selected value is also interesting as it can return solid granular packing which is relatively close to the fluid transition.

Sample packing. Subsequently, the sample packing needs to be selected. To these concern, one can decide among: pouring, growing particles and (random) packing generation. The first one consists of creating a packing, by means of pouring from a planar surface, the second implies that the code will first generate the centers of the particles and then build them by growing. The latter one (randomly) creates disks or spheres in a 2- or 3- dimension space and it is the selected one since it requires relatively less time-steps.

Simulation domain. A simulation domain is needed. One should bear in mind that, first, the volume should contain a representative number of elements and that the size of the simulation domain can imply that more computational power is needed (e.g. processors or "cores"), especially if bigger sizes are filled with very small particles. To this concern, using iterative test cases, using a setup with a cubical domain of 0.6 m per side and circa 4000 particles seem to define simulation that can last for no more than two days, which is considered acceptable on a nine-month long research. Secondly, such a domain is small enough to represent an infinitesimal volume of the Earth's crust can be considered at constant pressure and temperature (Fig.4.4). One the sizes are defined, two main types of boundary conditions, namely fixed boundary conditions and periodic boundary conditions (summarized in Table 4.3). On the one hand, fixed boundary conditions are real walls, with finite stiffness, on which any particle can overlap or bounce. On the other hand, periodic boundaries, are boundary conditions in which, a real wall is not created. Instead, if a particle impacts a periodic boundary at one side, in the next time iteration, it will enter from the opposite side with equal-in-intensity and opposite-in-sign velocity. On the other hand, fixed walls (or boundaries) are used to simulate experiments taking place in a closed cell or where the sample cannot be repeated in one direction. While the latter ones are more adopted in case one wants to simulate large granular domain which could be repeated in the periodic dimension.

The packing is allowed to freely deform in both x and y directions, therefore, periodic boundary conditions are selected in those axis, while the system is bounded by solid walls in positive and negative z directions. As two sub-region of spherical particles are desired, there should be an initial separator-wall which makes sure that two distinct layers are constructed. For this purpose, a double-layered wall is placed at the interface between the two regions, in such a way that the cube is cut into two halves, in z-direction. In addition, to make sure that particles are not inserted in a manner such that they might spillover the other layer, a 0.001 m gap between walls is added, which is declared as empty region. For consistency, each side of the wall has material properties of the adjacent layer.



Figure 4.4: Simulation domain. (Source: the Author)

Loading First, to obtain a solid sample with a stress condition lower than the lithostatic load of interest and with the highest isotropy possible, no external force is added during insertion [44].

A random generated packing (Fig.4.5) is then created. Subsequently to their insertion, particles relax in each layer layer relaxes in absence of gravity and the presence of the separator-wall, will prevent numerical errors from unexpected spillovers. Later, the division wall can be removed, letting particles lay on top of each other.

At this point, the sample is loaded with a typical lithostatic load described in Sect.2.2.

This load is the effective stress acting in negative z- direction, assumed to be equal to 10^7 Pa to simulate the typical lithostatic load during geological storage of CO₂. In continuum mechanics, this load is considered as a uniformly distributed load. As the present work deals with discrete elements, the load is applied including the discrete nature of the grains, therefore in the following manner (4.6).

- 1. The lithostatic load is applied on the upper face of the simulation domain, as in a real geological domain
- 2. Subsequently, a concentrated force can be obtained from it, by multiplying that load by that area. This returns a lithostatic force concentrated in its central point



Figure 4.5: Randomly generated sample.(Source: the Author)



Figure 4.6: Sample subjected to z-directed load. (Source: the Author)

3. It is assumed that some particle belonging to the cap rock, at distance from the top, lower than 1/5 of the height, are responsible for this force. Therefore, after the packing

relaxation, an additional force directed on the negative z-axis equal to the lithostatic force divided by the number of particles of that specific type.

4. The modeled lithostatic load is kept applied until the end of the simulation. Therefore, it serves two purposes. In the sample preparation it allows the sample to reach a stable stress condition. When the dissolution is activated, the load remains activated. This combination aims to model the geotechnical stress due to the lithostatic load, while the dissolution targets the grains.

In Table 4.2, specific characteristics for each simulation phase are presented. In the first phase, the initial goal is to create a solid, double-layered and isotropic sample. In this stage, the quantity of interest is the ration between kinetic and potential energy. Similarly, in the second phase, although the sample is relaxed, the removal of the separator-wall is likely to generate some new kinetics. For this reason, in this phase the sample is undergoing relaxation again, which is check by the same measure as the previous stage. For consistency, before applying the lithostatic load, it needs to be checked that the internal state of stress of the sample is lower than the load of interest. In a third phase, the goal is to recreate the loading which can be applied by the lithostatic load of interest. The goal, here, is to obtain a sample which, after loading, has a constant state of stress.

Input	Name	Length	Quantities	Averaging
Phase 1	Insertion + Relax	3000000	Kin., Pot.	bulk
Phase 2	Relax, no separator	3000000	Kin., Pot., Stress	bulk, per-cell
Phase 3	Loading	3000000	Stress	bulk, per-cell
Phase 4	Loading + shrinking	10000000	All	bulk, per-cell

Simulation phases

Table 4.2: Simulation phases.

Given the difference in Young's Moduli of the two materials, when calculating the timeincrement, the overlap can be firstly estimated as the maximum between the one provided by the Hertzian theory and 1% of the initial radius. Secondly, the maximum impact velocity between particles can be considered. At this point, one can define the smallest contact time, as depending on the collision between stiffest particles and the time-step is selected as 1/100 of the contact time. Given the input parameters, the time-step (or time-increment) adopted in the setup is equal to $\Delta T = 2 \ 10^{-7}$ seconds.

4.2 Modeling the dissolution

When the sample gets into a stable condition, the dissolution process is initiated. The dissolution is applied to every particle belonging to the porous media (Fig.4.7). In chemical formulas, related to real experiments, the dissolution is measured as a rate of mass loss by the solute over time, through a certain surface area. This rate is expressed as [45]:

Input	Name			
Timestep	Insertion + Relax			
Contact model	Hertzian			
Boundary x	periodic			
Boundary y	periodic			
Boundary z	fixed			

Simulation Information

 Table 4.3:
 Simulation phases.

$$\frac{dm_{loss}}{dt} = k_m A_m (1 - \frac{Q_m}{K_m}) \tag{4.3}$$

where k_m is the kinetic rate constant of the mineral (in [mol/(s-m²)]), A_m is the reactive surface area of the mineral (in [m² /kg_{water}]) per respective mineral and $(1-\frac{Q_m}{K_m})$ is a time dependent variable related to the saturation. The ratio $(\frac{Q_m}{K_m})$ defines the saturation state of the mineral. The mineral dissolves in the solution if the saturation state of the solution with respect to the mineral is lower than unity, and it can precipitate if the vice versa occurs. The term K_m is the equilibrium constant of the mineral defined as a function of temperature, whereas the term Q_m is called the ion activity product of the mineral, which is a function of the local concentrations of the involved aqueous species (e.g., for calcite H⁺, Ca²⁺, and HCO₃⁻) [46].

Calculating the remaining mass in the solute. It is now of interest to compute the remaining mass of each compound at a certain time, based on experimental values. In experiments the initial and final (at saturation) mass are declared. Then, to define the trend, a negative exponential function is the preferred, as it is the most common trend to describe concentration-related phenomena with high reactivity and low diffusivity, such as dissolution. Therefore, the following two conditions needs to be taken into account:

- The pre-exponential factor sets the maximum and the minimum values. At time zero, the mass must have the maximum value (its initial value), while at infinite time, the mass cannot go below a certain threshold, as saturation is reached.
- 2. In the exponential factor two variable appears, namely the turnover frequency and time. The first one is set as constant, while time is a free variable.

Considering such impositions, one can compute the remaining mass of each spherical particles in a packing in a two-folder manner. In one case, one could neglect the saturation. In this case, the remaining mass over time can be calculated as:

$$m_i(t) = m_{i,In} \exp\left(-\lambda_i t\right) \tag{4.4}$$

In the above-mentioned equation, $m_i(t)$ is the remaining mass of the solute at a certain time, which could be estimated from real experiments, λ_i is the i_{th} turnover frequency, for the i_{th} compound, and t is the time. The calculation of the turnover frequency is presented in the following paragraph.





In DEM, particles can deform (overlap), but cannot break. Therefore, one can model the dissolution of a particle as a particle reducing radius over time, which it is called shrinking particle or shrinking core model (Fig.4.8).

By assuming constant density over time, one can assume that any mass loss is equivalent to a shrinking in radius. Therefore, one can formulate Eq.4.4 as a function of radii obtaining Eq.4.5, in the case one would neglect the saturation.

$$r_i(t) = r_{i,In} \exp(-\lambda_i t) \tag{4.5}$$

with $r(t)_i$ being the remaining i_{th} particle radius, $r_{i,In}$ being the initial radius of particle i, λ_i being the turnover frequency calculated in Eq.4.6 and t being the time.

Turnover frequency. It is useful to understand how often the dissolution occurs. This implies to understand how often a certain quantity of compound is transfered into a solution by the solvent, which can be known by calculating the turnover frequency:

$$\lambda_i = k_{m,i} A_{m,i} P_{m.w.,i} l \tag{4.6}$$



Figure 4.8: Schematic representation of the shrinking particle model (Source: the Author).

Values for notable turnover frequencies are listed in Table 4.4. In the first column the values of kinetic rate constant, k_m , pertinent to geological storage of CO₂ are available in the literature. Regarding the reactive surface area, A_m , a reliable model adoptable for defining how the reactive surface area can evolve over time, is not yet available. Due to its complexity, it is often left as constant. In the present work, for simplicity, a reactive surface of reference can be estimated as equal to the totality of the area occupied by the smallest grain of the porous media. In the third and fourth column respectively, the molecular weight $P_{m.w.,i}$, is known for each compound, while the liters of solution can be calculated by knowing the density of the supercritical CO₂ and the initial volume of pores of the sample.

Ναμε	Ref.	$K_{m,i}$	A_m	$P_{m.w.,i}$	λ_i
Quartz	1.25 10 ⁻¹⁴	[47]	5.024 10 ⁻³	60.08	3.148 10 ⁻¹⁵
Calcite	5.01 10^{-10}	[48]	5.024 10 ⁻³	56.0774	1.4 10 ⁻¹⁰
Albite	6.92 10 ⁻¹¹	[12]	5.024 10 ⁻³	263.02	9.14 10 ⁻¹¹
Oligoclase	2.14 10 ⁻¹⁰	From CaO	5.024 10 ⁻³	265.42	2.85 10 ⁻¹⁰
K-feldspar	8.71 10 ⁻¹¹	[49]	5.024 10 ⁻³	278.33	1.22 10 ⁻¹¹
Kaolinite	$4.90 \ 10^{-12}$	[50]	5.024 10 ⁻³	258.16	6.35 10 ⁻¹¹
Dolomite	$6.46 \ 10^{-04}$	From CaO	5.024 10 ⁻³	184.4	5.94 10 $^{-04}$
Magnesite	$4.17 \ 10^{-07}$	[12]	5.024 10 ⁻³	84.31	1.76 10 ⁻⁰⁷
Dolomite	$6.46 \ 10^{-04}$	[12]	5.024 10 ⁻³	144.00	6.53 10 ⁻¹¹

Table 4.4: Calculation of notable turnover frequencies, in bold, the materials of interest for the present work

In case one would prefer to calculate the turnover frequency in respect to the moles of compound the molecular weight (third term of Eq.4.6) can be omitted. By knowing the kinetic rate constant, one can also calculate how often a unit of mass is going to react. This can be

expressed in term of turnover frequency, defined as the number of molecular reactions per unit of time.

Nevertheless, it should be noted that the turnover frequencies as calculated from Table 4.4, are calculated in respect to real experimental time, which can range from two weeks up-to months. As the present simulations are dealing modeling events happening in the order of the seconds, the original value of λ_i cannot be used, but a scaled turnover frequency needs to be introduced.

For numerical choices, the goal is to determine a turnover frequency where the difference between the initial and final i_{th} radius, named Δr , is smaller than the half of the most recurrent overlap, which is assumed to be $\delta_n = 10^{-5}$. Therefore, one can formulate:

$$\Delta r = \frac{\delta_n}{2} \tag{4.7}$$

which can be written as:

$$\Delta r = r_{i,In} - r_{i,In} \exp(-\lambda_i t) \tag{4.8}$$

iteratively, one compute that the condition $\Delta r \leq \frac{10^{-5}}{2}$, is satisfied for values equal to 10^{-16} and 10^{-18} , which are therefore utilized as turnover frequencies which represent carbonate-rich and silica-rich grains (from K-feldspars) in the simulations. Therefore Table 4.4 can be updated as Table 4.5

Ναμε	Ref.	$K_{m,i}$	A_m	$P_{m.w.,i}$	λ_i	$\lambda_{i,DEM}$
Quartz	1.25 10 ⁻¹⁴	[47]	5.024 10 ⁻³	60.08	3.148 10 ⁻¹⁵	
Calcite	5.01 10^{-10}	[48]	5.024 10 ⁻³	56.0774	1.4 10 ⁻¹⁰	10^{-16}
Albite	6.92 10 ⁻¹¹	[12]	5.024 10 ⁻³	263.02	9.14 10 ⁻¹¹	
Oligoclase	2.14 10 ⁻¹⁰	From CaO	5.024 10 ⁻³	265.42	2.85 10 ⁻¹⁰	
K-feldspar	8.71 10 ⁻¹¹	[49]	5.024 10 ⁻³	278.33	1.22 10 ⁻¹¹	10^{-18}
Kaolinite	4.90 10 ⁻¹²	[50]	5.024 10 ⁻³	258.16	6.35 10 ⁻¹¹	
Dolomite	$6.46 \ 10^{-04}$	From CaO	5.024 10 ⁻³	184.4	5.94 10 ⁻⁰⁴	
Magnesite	$4.17 \ 10^{-07}$	[12]	5.024 10 ⁻³	84.31	1.76 10 ⁻⁰⁷	
Dolomite	$6.46 \ 10^{-04}$	[12]	5.024 10 ⁻³	144.00	6.53 10 ⁻¹¹	

 Table 4.5: Calculation of notable turnover frequencies, in bold, the materials of interest for the present work

Advantages of the shrinking particle model. The first advantage of this model is its compatibility with real experiments, as one can convert the mass concentrations from the experiments in radii. In experiments, the initial mass of a sample and the percentages in weight of each compound (in the sample), are always declared. This returns the initial mass. Then, after the experiment is conducted the final mass loss by each compound at saturation can be calculated. Now, one knows how much compound (SiO₂ and CaO are

considered in our research), are present in the solid compound (or sample), before and after the dissolution has taken place. Now one can assume that each compound of the sample is spherical and is homogeneous. Therefore, it is assumed that SiO_2 and Calcium-Oxide are the only compound of each particle. It is also assumed that if a particle is dissolving in a solvent, this can be seen as a particle that reduces in spherical volume, keeping constant volume. In other words, any mass loss can be compared to a radii reduction in time.

Chapter 5

Simulation results

The DEM-based methodology presented in the previous section is now applied. Summarizing, the DEM simulations are conducted creating a cubical domain of sides equal to 0.6 meters per side, defining periodic boundary conditions in either positive or negative x- and y- directions, while real walls bound the simulations in both z- directions. This domain is initially divided into two regions. The top one is dedicated to the representation of the particles defining the caprock, while the lower one hosts the modeling of the porous media. The caprock is modeled as a set of particles characterized by Young's Modulus equal to 10¹¹ Pa, cohesion between particles expressed by a cohesion energy density equal to 2000 Pa, and radii ranging from a minimum of 0.015 meters to a maximum of 0.018 meters. The porous media is modeled as a variable combination of two species. The first one, representing carbonate-grains, is characterized by a Young's Modulus equal to 10⁹ Pa and radii ranging from a minimum of 0.02 meters to a maximum of 0.02 meters. The second represents silicagrains and is characterized by a Young's Modulus equal to 10¹⁰ Pa and radii ranging from a minimum of 0.025 meters to a maximum of 0.028 meters. The characterization is based on Calcite (CaO), for carbonates, and K-feldspars (KAISi₃O₈) for silicates.

In both regions particles are spherical, smooth and homogeneous, with constant density equal to 2700 kg/m³, the poisson ratio is equal to 0.35, the coefficient of restitution is equal to 0.8 and the coefficient of static friction is equal to 0.35. In both regions the initial volume fraction is set to be 0.62.

Since the interest of the research is to observe how micro-mechanisms in the REV are changing according to different mineralogies, the varying parameter is the quantity of carbonateand silica-grains in the porous media. Therefore, the porous media can be defined by five possible mixtures, expressed as percentages in weight, ranging from 100% silicate vs. 0% carbonate, to 0% silicate vs. 100% carbonate, with three mixed conditions in between, namely 25% vs. 75%, 50% vs. 50% and 75% vs. 50%. Firstly, a pre-failure situation is modeled. The goal is to prepare a REV that, at the end of it preparation phase, exhibits a ratio between kinetic and potential energies stably equal or lower than 10^{-6} , a stably constant value of internal stress different than zero and a coordination number major or equal than 4. This controlling quantities are measured in each bulk.

In this phase, particles of each specie are firstly inserted in each designed region, allow-

ing an initial mutual overlap and with no gravity. Secondly the whole sample undergoes relaxation, meaning that no force is added to the particles. Thirdly a lithostatic load of 10^{Pa} directed in negative z-direction of 10^7 Pa is applied.

Secondly, the interest shifts towards to the failure analysis of the REV. With the lithostatic load kept active, dissolution is then applied to both, particle species belonging to the porous media. Dissolution is modeled by describing a spherical particle shrinking over time, at a certain frequency (called turnover frequency) and with a negative exponential trend. Each particle specie is characterized by a specific turnover frequency which can be calculated. The two turnover frequencies, are $\lambda = 10^{-16}$, for carbonates and $\lambda = 10^{-18}$ for silicates.

In the attempt of seeking possible failure of the REV, the interest is to observe its variation in bearing capacity. In particular, the goal is to seek if the caprock can collapse by means of shrinking particles belonging to the porous media. To understand if this is possible, a first configuration neglects saturation and let particles shrinking with no threshold. In a second phase, the limit offered by the saturation is included, to model a more realistic case. These two configurations are called unlimited- and limited-shrinking, respectively. During the latter phase, two types of averaged quantities are adopted, namely, bulk-averaged and per-cell averaged.



Figure 5.1: Summary of the DEM packing

5.1 Pre-failure behavior

In this section, the results of the pre-failure study are presented. In Fig.5.2 the phases included in this study are summarized, recalling the REV characteristics.

Energy. The first quantity that is analyzed is the ratio between kinetic and potential energies, which can be used as check to understand when the system reaches stability. Values



Figure 5.2: Summary of DEM simulations in pre-failure study. Simulation phases comprised REV characteristics are also highlighted. (Source: the Author).

are presented in Fig.5.3. Shifting towards the analysis of the caprock, one can see that the caprock starts with practically the same trend with all cases as there is only one possible mixture. Nevertheless, looking carefully, small deviation can be perceived due to slight different atom counting. The volume fraction and the boundary conditions are the same as in the porous media, therefore, after an initial fluctuation, the coordination number reaches a value which is higher than four, which is one of the signature of solid packing. Subsequently, as there is no force added to the packing, kinetic gradually decreases and the coordination number becomes stable.

Contacts. Secondly, the analysis can turn to the coordination number of the two bulks, which is depicted in the graphs of Fig.5.4. The analysis starts with the porous media. In the initial phase, when particles are inserted a fluctuation can be observed. This is due to the fact that particles are inserted with an initial overlap. Since a repulsive force is generated by such overlap, some kinetics are initially generated, until an equilibrium is found. fter an initial fluctuation, the coordination number reaches a value which is higher than four, which is one of the signature of solid packing. It seems clear that all mixtures lead to similar coordination numbers within the porous media. Since the system has no force applying on the particles, once the equilibrium is found by particles in the porous media, there is almost no reason for particle to change in kinetics, which explains the constant trend that follows.

In the moment the separator-wall is removed the porous media, seems to acquire more contacts, which can be seen from a increase in the coordination number. In this phase, co-ordination number seems to grow if the porous media contains a higher quantity of carbonate grains, since carbonates are softer material than the silicates. As in the previos phase, new kinetics are generated, in this case by the removal of the separator-wall. Proceeding with the simulation, this coordination number reaches a plateau after the wall is removed since, no additional force are yet inserted.

When the load is instantaneously applied, all mixtures of porous media return a increase in the coordination number. It is notable that the higher is the percentage of carbonate-grains in the porous media, the higher is the drop. This is, once again, linked to the fact that the carbonate- grains have lower stiffness. There seem to be a neat dependency between the amount of silicate- and carbonate- grains during the loading phase, as every increase in the

quantity of carbonates in the porous media, corresponds to a higher trend in the coordination number.

When the separator-wall is removed, the bulk of the caprock immediately loses contacts as depicted by the downward drop in coordination number. In this phase it is clear that the stiffer the porous media is, the smaller is this drop. In fact, one can see that porous media that is only comprising silicate- grains have little gap, while this is bigger the more carbonate-grains are inserted into the porous media. It seems that, when the separator-wall is removed, the porous media is generally gaining new particles. Nevertheless, the stiffer the porous media becomes, the smallest this migration becomes. When the loading is applied to the REV, in with every mixture in the porous media, the caprock increases in terms of coordination number. It seems clear that when the packing is subjected to the loading, the softer the porous media is, the slower the caprock is gaining contacts. This is once again linked to a matter of stiffness. From a qualitatively analysis of the coordination number in the loading phase, it seems that the caprock is again tending to go downwards in a quasi- rigid fashion and the softer the porous media becomes, the slower contacts between particles of the caprock increase.

Stress. Further on, one can shift to the analysis of the stress in the two bulks, which is conducted in terms of the hydrostatic component $\sigma_z z$ of the stress tensor, is depicted in the graphs of Fig.5.5. In the initial phase, the porous media with stiffest material shows the highest stress in its bulk. In fact, one can see that diminishing the quantity of silicate-grain, which have higher Young's Modulus and increasing the quantity of carbonate-grains, the stress tends to progressively diminish. With all mixtures it is possible to achieve a stable condition of stress different than zero, which is one of the signs indicating solidity of the sample. This is also linked to the lack of added forces. The only force generated within the sample is the one created by the initial overlap. By its formulation, the stress tensor depends on the contact force and on the leverage generated between two particles. When the packing has found equilibrium, the two quantities affecting the stress tensor tend to remain constant, therefore, a constant stress is obtained.

When separator-wall is removed, all mixtures within the porous media are subjected to a raise in the stress. Again, as no additional force is added to the packing, an equilibrium in the stress can be found. In the moment the lithostatic load is applied, it seems that all mixtures lead to a certain increase in the stress. It seems that the more silicate-grains is added in the porous media, the smaller the jump is. Since the carbonate-grains are softer particles, it is expected that, when subjected to a load, their bulk can be more easily penetrated compared to a stiffer silicate-grain-rich one. In the third phase, after the load is applied, one can see that all mixtures in the porous media lead to a stable stress configuration. This is expected, since the load is constantly applied. Therefore, after the initial fluctuation, the bulk can find its preferred stable condition.

In the caprock, a stable stress configuration different than zero, is reached in the initial phase. The value of the stress derives from very stiff particles which are initially overlapping, therefore, a relatively high contact force can contribute to the stress computation. After a

stable configuration is reached, when the separator-wall is removed, the bulk of the caprock seems to diminish in stress. By confronting this with the same trend in the porous media, it seems that while particles are loss by the caprock, new particle are acquired by the porous media. Nevertheless, when the porous media has higher composition in silicate-grains, this gap seems to be reduced, as the stiffer material offer more resistance to compenetration from the upper layer.

Therefore, more atoms with active contacts enter the porous media and exit the caprock, leading to a decrease in the averaged stress in the latter one. In the last phase, a small drop is perceived by the caprock, since, once again, particles have the chance to leave the bulk, in a trend that is similar to the one in the previous phase.

The deviatoric stress is checked as part of the stress tensor, also for understanding the consitency of the stress calculation during the loading phase.

5.1.1 Averaged - Per- Cell - quantities

In LIGGGHTS, once the particles are assigned to a group, it is possible to measure microscopic quantities for the whole simulation. Nevertheless, when one desires to average, the region where the particles are defined remains the same. In more sophisticated terms, in LIGGGHTS it is not possible to create a dynamic region, but only a static region. On the one hand, these simulations are quasi-static, therefore this lack should not create great deviation. Nevertheless, in an attempt to use coarse graining, one can define smaller domains contained in the REV where it is possible to average some control quantities such as particle radius, velocity, volume fraction and pressure. Ideally, by using a smaller domain, one can reduce computational mistakes while averaging. LIGGGHTS is let free to decide upon the amount of cubic cell that one can create. The software requires a cutoff to define the size of the cells and subsequently how many. By inserting the smallest cutoff possible, which is 3, the presented REV can be divided in 27 cells. In this research, three regions are selected, namely the ones with center of mass with coordinates equal to X = Y = 0.3 m and Z = 0.1, 0.3 and 0.5. These regions are called as from the output names from LIGGGHTS, which are region 5 (the lowest), region 14 (the middle one) and region 23 (the top one).

These are the results of the control quantities averaged in region 5:

Radius. As from Fig.5.7, in the first phase, the average radius in the cell diminishes if more silicate-grains are inserted and diminishes if with increasing the quantity of carbonates. This is consistent with the radius input at the beginning of the simulation. In the next phase, when the wall is removed, all averaged radii remains constant, as there is no reason for them to change. In the third phase, right after the load is applied there seem to be a very little drop and then a stable trend. This is due to the elastic response of the spherical particles after the load.

Velocity. As from Fig.5.8, during the first phase the average velocity seems to be low and with a decreasing trend which is almost reaching zero. This means that the kinetic is constantly decreasing, defining an increasing stable region. When the separator-wall is removed, the velocity seem to increase more if the porous media comprises more carbonate-grains than silicates. When the division is removed, the gap comprised in the separator-wall is filled with particles which can come from both layers. This creates kinetic, until a peak is achieved. In this phase it seems that the highest peak is achieved when the porous media is made of only carbonates, while the lowest is reached when only silicates are present.

In the third phase, when the lithostatic load is applied, all mixture seem to enhance a raise in velocity. In particular, the mixture completely made of carbonates seems to reach the highest peak, while the mixture comprising only silicates, gives rise to almost no change in velocity. Diversely from the previous phase, by changing a percentage of the mixture does not imply a linear change in the peak. At the end of the phase, all velocities seem to go to a value close to the zero.

Volume fraction. As from Fig.5.9, initially, the volume fraction is very similar to the value of

0.62 which is the input for the bulk. It seems that when the porous media is mostly comprised of silicates, the volume fraction in the region is the highest, nevertheless there is not visible link between the amount of carbonates or silicates and the trend of volume fraction in this region. When the separator-wall is removed, one can see three trends. If the porous media contains only silicates, the volume fraction remains practically constant (only a very small drop is perceived). Secondly, the 50%-50% combination, seem to have a decreasing drop. Thirdly, the remaining combinations of mineralogies raise in volume fractions. The random distribution of the particles might have a role. Anyway towards the end of the phase, all mixtures lead to a stable value. When the lithostatic load is applied, it seems that the region experiences an raise in volume fraction, in all cases but when the porous media is only comprised of silicates. In all the other cases, it seems that the amount of carbonates is responsible for a raise in volume fraction.

Pressure. As from Fig.5.10, in the initial phase, the region shows higher pressure if the amount of silicates increases. This is due to the higher stiffness of the silicates compared to the carbonates, which returns into higher contact force, therefore higher pressure. When the wall is removed, all mixture seem to lead to different trends. Anyway, all of them lead to a stable condition of pressure towards the end of the phase. When the lithostatic load is applied, all mixtures seem to rise. In the case of only silicates in the porous media, it seems that the previous stress condition is already close to the maximum compression possible and now the increase in pressure is very small. This is mostly due to the pressure. In fact, during the loading, the other mixture are subjected to a raise in pressure. This is possible since, softer particles offer bigger compenetration. Subsequently more particles in contact are acquired by the region, with a subsequent increase in pressure. Vice versa, when the porous media is fully comprised of silicates, the opposite behavior seem to occur.

These are the results of the control quantities averaged in region 14:

Radius. As from Fig.5.11, the numbers of the volume fractions in the initial phase indicates the presence of particles belonging to either the caprock or the porous media. When the porous media is filled only with silicates, the averaged radius seems to be higher, meaning that more particles of the porous media are present. By increasing the quantity of carbonates, the average decreases, indicating a prevalence of particles belonging to the caprock. In a second phase, when the separator-wall is removed, one can see that the averaged radius decreases with a sharper trend if the porous media is rich of silicates. This can depend on the similarity of stiffness between particles at the interface. Towards to the end of this phase, the region seems to reach a stable value for all the mixtures in the porous media. When the lithostatic load is applied, if the porous media is comprised of only silicates, an increase in the averaged radius is perceived. In all other cases, the trend is the opposite. This is the result of the reaction of the material when loaded. When the porous media made of only silicates is loaded, it seems that it is first compressed and then, with its elastic response, it is able to recover its original configuration more than in the other mixtures. In fact, when the other mixtures are adopted, the averaged radius decreases, indicating higher tendency of the caprock in rigidly entering in the porous bulk. Towards to the end of this phase, all mixtures, lead to a stable configuration in averaged radius.

Velocity. As from Fig.5.12, during the first phase the average velocity seems to be low and with a decreasing trend which is almost reaching zero. This means that the kinetic is constantly decreasing, defining an increasing stable region. When the separator-wall is removed, the velocity seem to increase more if the porous media comprises more carbonate-grains than silicates. When the division is removed, the gap comprised in the separator-wall is filled with particles which can come from both layers. This creates kinetic, until a peak is achieved. In this phase it seems that the highest peak is achieved when the porous media is made of only carbonates, while the lowest is reached when only silicates are present.

Volume fraction. As from Fig.5.13, the averaged volume fraction is initially constant. When the separator-wall is removed, three trends occurs. When the porous media is only comprised of silicates, there is a small drop, while when the 50%-50% combination is inserted an increase is perceived and when the other mixtures are adopted, a decrease occurs. This is probably due to the random creation of the packing. Anyway, all the mixtures return stable values going towards to the end of the phase. When the load is applied, all mixtures, generate a raise in volume fraction. In particular, it seems that when the silicates prevail, the raise is slower than when the carbonates are predominant. Towards to the end of the phase, a constant trend is perceived.

Pressure. As from Fig.5.14, in the initial phase, the pressure averaged in the cell, seem to be affected by the stiffness of the material. One can see that when the silicates are predominant, the pressure is higher, which is due to the presence of stiffer material in the region. After a constant trend is achieved, the separator-wall is removed. It seems that the presence of carbonate leads to a drop towards similar values. Contrarily, when the porous media is only comprised on silicates, the trend seems similar, but the final value is higher. A constant trend follows in the phase, for all mixtures. When the loading is applied, if the porous media is only comprised of silicates, the region seems to have almost no increase of pressure. Contrarily, when the carbonate-grains are included, pressure can increase, due to lower stiffness. A stable trend follows for the rest of the loading phase.

These are the results of the control quantities averaged in region 23:

Radius. As from Fig.5.15, in the upper layer, during the first phase, the averaged radii indicates a prevalence of caprock, as required by the input. When the separator-wall is removed, the region seem to have mixed trends. If the porous media is only comprised of silicates, the averaged radius is increasing. The vice versa happens with only a mixture of only carbonate inserted. The other mixtures in between have random trends. After the change, a stable quantity is always achieved. When the packing is loaded, with only carbonates in the porous media, the region suddenly acquires a bigger averaged radius, which is still belonging to the caprock range. It seems that the elastic response of the porous media, can alter the particle concentration.

Velocity. As from Fig.5.16, the velocity is almost negligible in the first two phases. In the

third phase one can see that, loading the packing with a purely silicate porous media does not alter the averaged velocity of region 23. In case of increased amount of carbonates, an increase in velocity is perceived. This is due to the difference in the Young's Modulus offered by the different porous media.

Volume fraction. As from Fig.5.17, the per-cell volume fraction is higher with only silicates in the porous media. When the separator-wall is removed, an initial drop in every combination is followed by a stabilization. In a third phase, when the load is applied, the more the carbonate mix is increasing in the porous media, the more the cell decreases in volume fraction. This depends on the difference in the Young's Modulus between the mixtures.

Pressure. As from Fig.5.18, the pressure is initially higher when the porous media is rich in silicates. When the wall is removed, if the porous media is rich in silicates, a slower drop is perceived compared to the other mixtures. This is once again, responsibility of the different Young's Modulus between mixtures. After a plateau is reached, when the load is applied, carbonate-rich mixtures allow a bigger decrease in volume fraction, while the porous media rich in silicates, lead to a stable value during loading.

5.2 Failure behavior

Now, the DEM-methodology is applied to check if failure in the representative element of volume can be perceived. The goal here, is to apply the mineral dissolution to the porous media, which intended as shrinking of the particles belonging to the porous media, while the lithostatic load is remaining constantly active on the REV. subsequently, the dissolution with unlimited shrinking in a 0,6 m cubical box is presented. Particles of the porous media, undergo a shrinking with a negative exponential trend with a turnover frequency that is equal to 10^{-16} for particles representing carbonate-grains, and 10^{-18} for particles representing silicate-grains. This case falls into the unlimited shrinking case, as the radius can shrink towards to the zero, as the limit imposed by the saturation is neglected.

5.2.1 Test case: Reduced box

In a raising complexity, it is first desired to define it the collapse is possible, by means of a test case, with a smaller simulation box. This can give failure-related information in an optimized simulation time. The same structure used for creating the REV is adopted. The same boundary conditions adopted for the REV are adopted in this test case, namely, periodic boundary conditions are set in both x- and y- directions, while real walls are bounding the simulation domain in both z-directions.

This domain is initially divided into two regions. The top one is dedicated to the representation of the particles defining the caprock, while the lower one hosts the modeling of the porous media. The caprock is modeled as a set of particles characterized by Young's Modulus equal to 10^{11} Pa, cohesion between particles expressed by a cohesion energy density equal to 2000 Pa, and radii ranging from a minimum of 0.015 meters to a maximum of 0.018 meters. The porous media is modeled as a variable combination of two species. The first one, representing carbonate-grains, is characterized by a Young's Modulus equal to 10^9 Pa and radii ranging from a minimum of 0.02 meters to a maximum of 0.02 meters. The second represents silica-grains and is characterized by a Young's Modulus equal to 10^{10} Pa and radii ranging from a minimum of 0.025 meters to a maximum of 0.028 meters. The characterization is based on Calcite (CaO), for carbonates, and K-feldspars (KAISi₃O₈) for silicates.

In both regions particles are spherical, smooth and homogeneous, with constant density equal to 2700 kg/m³, the Poisson ratio is equal to 0.35, the coefficient of restitution is equal to 0.8 and the coefficient of static friction is equal to 0.35. In both regions the initial volume fraction is set to be 0.62.

Initially, knowing that the interest of the research is to observe how micro-mechanisms in the REV are changing according to different mineralogies, a fixed quantity of carbonate- and silica-grains in the porous media is selected. Therefore, the porous media can be initially defined, via percentages in weight, as a 50% silicate vs. 50% carbonate- mixture.

Hereby, the results of the simulation adopted using an unlimited shrinking model, in a cubical box of 0.3 meter per side, are presented. Two turnover frequencies equal to 10^{-15} and 10^{-17} , are initially selected.

Contacts. Immediately after the activation of the shrinking, the particles placed in the porous media starts loosing contacts, as notable from a gradually decreasing coordination number after the third black dotted line. After an initial drop, the coordination number seems to fluctuate around a value close to 4. At time equal 10 second, it is visible that the porous media as drastically dropped below 4. This is followed by a series of fluctuations and drops below 4. It is known that sample packing with coordination number below 4, has the chance to behave more like fluids than like solids. This could happen here.

Analyzing the caprock, a sort of similar trend occurs. When the shrinking of the particles is applied, there is no such steep drop as in the other layer. The coordination number starts fluctuating and suddenly becomes lower than 4. This seems to be followed by, a fluctuation around the threshold of 4, which is followed by an amplified oscillation, until, at a certain point, the packing seems to be able to recover a value bigger than four. This is only temporary, as the coordination number seems to be stable, with sudden drops and raise, probably linked to some elastic response.

It seems that, with the current parameters, a drop in the coordination number of particles belonging to the porous media, is accompanied to a the same in the caprock. It seems that the fluctuations in the coordination number of the porous media, can lead to a raise-and-loss trend in the caprock. This can be symptomatic of a collapsing caprock over a dissolving porous media.

Energy. As notable in Fig.5.19, as soon as the dissolution is activated, an instantaneous raise in kinetics is perceived. From that moment on, there seem to be no stability in none of the layers, as the ratio of kinetic over potential energy, is constantly floating and increasing. This means that the bulk does not have the chance to become stable during the dissolution process, but particles are characterized by high kinetics.

Stress. As notable from 5.22, when the dissolution is applied, it seems that a gradually decreasing number of contacts is responsible for a gradual reduction in the stress, in the porous media. After the drop seems to be concluded, a quasi-stable configuration seems to be found. This is mostly due to the exponentially negative trend of shrinking. At some point, it seems that there is a raise in the stress again. This is most likely to be due to the caprock being able to suddenly enter into the porous media bulk. In other words, there is a possibility of observing a collapse of the caprock, by observing a drastic drop in stress in the porous media. A very constant decrease in stress follows, this is due to the unlimited shrinking.

The caprock layer starts decreasing in stress, in a trend which is very similar to the porous media. It seems that while the porous media is shrinking, the caprock is gradually loosing contacts between similar grains. This lack of contacts can be responsible to a decreasing stress. Similarly to the porous media, the caprock seems to find a temporary stable configuration, but it keeps decreasing over time. It should be noted that the stress in the caprock is calculated over the volume of its initial region. When using the built-in functions in LIGGGHTS, to average the stress in the caprock bulk, the volume of reference is always the region where the particles of the caprock are first inserted. In the case of particles invading the porous media, the region of reference should be adapted, which does not seem to be

possible in LIGGGHTS. If particles with active contacts are loss by the caprock because they invade the porous media, a decreasing stress should be perceived, since less contact forces are contributing to the calculation, while the volume is fixed. The deviatoric stress depicted in Fig.5.22, shows a porous media which is visibly decreasing is shear strength as soon as the shrinking is activated. A clearly visible drop is perceived from the graph. After this phase, there is no trace of a constant trend, as the deviatoric stress constantly fluctuates in a random fashion.

The porous media seems to have a similar fashion with smaller fluctuations. Contrarily to the porous media, there is a point when the caprock is actually increasing in its deviatoric stress. Nevertheless, this is followed by a new drop afterwards.

Now, another test-case in a reduced sample is conducted, using two turnover frequencies equal to 10^{-16} and 10^{-18} , respectively.

By using a combination of turnover frequencies equal to 10^{-16} and 10^{-18} for the two types of particles in the porous media, there seem to be a much docile drop, which can be due to the negative exponent which becomes extremely close to zero, indicating a dissolution which is much slower then the previous case. Within this gradual loss, the porous media has sporadical peaks. At some point, there seem to be a drastic lack of contacts, which fuses a fluctuating coordination number. This trend does not seem to stop.

In the caprock, the coordination number is almost the same as in the preparation phase, remaining above the threshold equal to 4. Nevertheless, when the porous media seem to present drops in coordination number, the cap rock follows. In the same moment the porous media has lost a stable trend, the caprock follows again. From this moment, the caprock starts fluctuating in the same fashion as the porous media, but reaching a value which is below the threshold of 4. From the moment the shrinking is applied, Fig.5.23, shows that the porous media is not stable anymore as important kinetics are activated. For the whole shrinking, there is not trace of slowing down in kinetics, meaning that the more the dissolution proceeds, the more the porous media particle tend to accelerate. In particular, at time 10 seconds, a further peak is perceived, suggesting that the loss of contacts has reached a critical value. The same trend occurs for the caprock. Stress depicted in Fig.5.25, highlights that as soon as the dissolution is activated both layers are decreasing in stress (the zz hydrostatic component is reported in the figure). The two trends seem to be very similar until, at time 10 seconds, a drop is perceived. This is followed by a new drop downward.

5.3 Failure mode: Unlimited accelerated shrinking

Here, the goal is to determine the presence of a failure, in particular an eventual rapid movement of the caprock that can be compared to collapse. Quantities that can be outputted in the smaller cells can be of added value for this step, since LIGGGHTS, does not offer averaging of region that "follow" the movement of the particle. In this configuration, the goal is to first set an unlimited shrinking, which the selected way of modeling particle dissolution, neglecting the limit imposed by the fluid saturation. This is of geotechnical relevance. In fact, by shrinking the particles in such a manner that the particle disappear, can give insights about the most likely failure. In other words, the structure of caprock and porous media is deliberately subjected to unlimited shrinking in order to observe its micro-mechanical behavior, in the event of an extreme perturbation.

This domain is initially divided into two regions. The top one is dedicated to the representation of the particles defining the caprock, while the lower one hosts the modeling of the porous media. The caprock is modeled as a set of particles characterized by Young's Modulus equal to 10^{11} Pa, cohesion between particles expressed by a cohesion energy density equal to 2000 Pa, and radii ranging from a minimum of 0.015 meters to a maximum of 0.018 meters. The porous media is modeled as a variable combination of two species. The first one, representing carbonate-grains, is characterized by a Young's Modulus equal to 10^9 Pa and radii ranging from a minimum of 0.02 meters to a maximum of 0.02 meters. The second represents silica-grains and is characterized by a Young's Modulus equal to 10^{10} Pa and radii ranging from a minimum of 0.025 meters to a maximum of 0.028 meters. The characterization is based on Calcite (CaO), for carbonates, and K-feldspars (KAISi₃O₈) for silicates.

In both regions particles are spherical, smooth and homogeneous, with constant density equal to 2700 kg/m³, the Poisson ratio is equal to 0.35, the coefficient of restitution is equal to 0.8 and the coefficient of static friction is equal to 0.35. In both regions the initial volume fraction is set to be 0.62.

The varying parameter is the quantity of carbonate- and silica-grains in the porous media. Therefore, the porous media can be defined by five possible mixtures, expressed as percentages in weight, ranging from 100% silicate vs. 0% carbonate, to 0% silicate vs. 100% carbonate, with three mixed conditions in between, namely 25% vs. 75%, 50% vs. 50% and 75% vs. 50%.

The two turnover frequencies, are the realistic values from Table 4.5. The values are $\lambda = 1.4$ 10^{-10} for carbonates and $\lambda = 1.22 \ 10^{-11}$ for silicates.

Hereby, the results of the simulation adopted using an unlimited shrinking model, in a cubical box of 0.6 meter per side, are presented. Two turnover frequencies equal to $1.4 \ 10^{-10}$ and $1.22 \ 10^{-11}$, are initially selected.

Energy. As from fig.5.43, when the shrinking is applied, the trend keeps decreasing with a slightly different curve. The mixture with higher percentage of carbonate, return an energy ratio which is a higher. Increasing, the quantity of silicates seem to speed up the drop. *Coordination Number.* As from fig.5.44, when the dissolution is activated, all coordination

numbers in the porous media are drastically going towards the zero, which is expected due to the non-natural dissolution rate. Porous media with higher percentage of carbonate-grains seems to keep a slight higher value, while the opposite happen for silicate- rich porous media. A clear point of collapse of the porous media is not visible, but it can be qualitatively understood that there is collapse. Looking at the caprock, its coordination number does not seem to change during dissolution. This suggests the possibility of rigid collapse of the caprock on the porous media. *Stress.* As from fig.5.45, the stress decreases in all combinations of porous media, while the caprock seem to keep the same value during shrinking. A key element seem to be the quantity of carbonates, which appears to slow down the decrease in stress, while the presence of silicates enhancing it. As from fig.5.46, the deviatoric stress always drops during dissolution. In the porous media, a composition rich in silicates, seem to slow down the drop. Qualitatively, in the porous media, this quantity is always firstly fluctuating and the decreasing, but no clear correlation with the mineral composition in the porous media is notable.

Regarding the behavior of the region 5, during shrinking:

- 1. Radius. As from Fig.5.31. it seems that the average particles all particles shrink towards radius equal to zero as required
- 2. Velocity. As from Fig.5.32, a mixture rich in carbonates leads to higher kinetics during dissolution
- 3. Volume Fraction. As from Fig.5.33, the volume fraction goes towards the zero in a trend determined by the prevalent mineralogy
- 4. Pressure. As from Fig.5.34, pressure is decreasing but is higher with silicates-rich porous media. The other mixtures lead to a different trend

Regarding the behavior of the region 14, during shrinking:

- 1. Radius. As from Fig.5.35 it seems that the average particles is reducing without going to zero, since also particles of the caprock are in the region
- 2. Velocity. As from Fig.5.36, during dissolution, porous media with high concentration of carbonates seems to allow higher velocities
- 3. Volume Fraction. As from Fig.5.37, all volume fractions seems to decrease. The porous media therefore, determine this trend
- 4. Pressure. As from Fig.5.38, pressure is always decreasing. Silicates-rich porous media lead to a sharper and lower drop

Regarding the behavior of the region 23, during shrinking:

1. As from fig.5.39, it seems that the average particles is reducing without going to zero, if the porous media is rich in carbonates.

- 2. As from fig.5.40 during dissolution, porous media with high concentration of carbonates seems to allow higher velocities
- 3. As from fig.5.41 all volume fractions seems to decrease. The porous media therefore, determine this trend
- 4. As from fig.5.42 pressure is always decreasing. Silicates-rich porous media lead to a sharper and lower drop

5.4 Failure mode: Unlimited scaled shrinking

The DEM-based methodology presented in the previous section is now applied. Summarizing, the DEM simulations are conducted creating a cubical domain of sides equal to 0.6 meters per side, defining periodic boundary conditions in either positive or negative x- and y- directions, while real walls bound the simulations in both z- directions. This domain is initially divided into two regions. The top one is dedicated to the representation of the particles defining the caprock, while the lower one hosts the modeling of the porous media. The caprock is modeled as a set of particles characterized by Young's Modulus equal to 10^{11} Pa, cohesion between particles expressed by a cohesion energy density equal to 2000 Pa, and radii ranging from a minimum of 0.015 meters to a maximum of 0.018 meters. The porous media is modeled as a variable combination of two species. The first one, representing carbonate-grains, is characterized by a Young's Modulus equal to 10^{9} Pa and radii ranging from a minimum of 0.02 meters to a maximum of 0.02 meters. The second represents silicagrains and is characterized by a Young's Modulus equal to 10^{10} Pa and radii ranging from a minimum of 0.025 meters to a maximum of 0.028 meters. The characterization is based on Calcite (CaO), for carbonates, and K-feldspars (KAISi₃O₈) for silicates.

In both regions particles are spherical, smooth and homogeneous, with constant density equal to 2700 kg/m³, the poisson ratio is equal to 0.35, the coefficient of restitution is equal to 0.8 and the coefficient of static friction is equal to 0.35. In both regions the initial volume fraction is set to be 0.62.

In the attempt of seeking possible failure of the REV, the interest is to observe its variation in bearing capacity. In particular, the goal is to seek if the caprock can collapse by means of shrinking particles belonging to the porous media. To understand if this is possible, a first configuration neglects saturation and let particles shrinking with no threshold. In a second phase, the limit offered by the saturation is included, to model a more realistic case. These two configurations are called unlimited- and limited-shrinking, respectively. During the latter phase, two types of averaged quantities are adopted, namely, bulk-averaged and per-cell averaged.

In this section results from the DEM simulations, using a numerically-scaled turnover frequency are presented. A representative element of volume is adopted, with a cubical box of 0.6 meters per side, and periodic boundary conditions in both x- and y- directions. Real walls are placed to bound the simulations in positive and negative z-directions.

The varying parameter is the quantity of carbonate- and silica-grains in the porous media. Therefore, the porous media can be defined by five possible mixtures, expressed as percentages in weight, ranging from 100% silicate vs. 0% carbonate, to 0% silicate vs. 100% carbonate, with three mixed conditions in between, namely 25% vs. 75%, 50% vs. 50% and 75% vs. 50%.

The two turnover frequencies, are $\lambda = 10^{-16}$ for carbonates and $\lambda = 10^{-18}$ for silicates. The dissolution is applied with an unlimited shrinking, meaning that the effect of fluid saturation is still neglected, therefore, particles are free to shrink completely.

5.4.1 Results

Energy. During the shrinking of the particles, it seems that increasing the quantity of silica the in the porous media, it is possible to have apparent stable ratio during the dissolution. This trend does not happen with the other mixture. Once again there is a link between energy and stiffness of the material.

Contact. During the dissolution phase it seems that when the porous media gets dissolved, high quantity of silicates allows a long lasting stable coordination number equal to 5. Carbonates also reach this value but in a slower trend.

Stress. Almost no change in the stress is perceived.

Regarding the behavior of the region 5, during shrinking:

- 1. Radius. As from Fig.5.47, the more the silicates comprise the porous media, the more the region exhibits higher averaged radius. This means that the region has better chances to be predominated by porous media, if more silicates are inserted.
- 2. Velocity. As from Fig.5.48, although the velocity seems to be very slow, highest kinetics are enhanced by a porous media, reach in carbonates. Due to their lower stiffness, they allow more compenetration of particle of the caprock.
- 3. Volume Fraction. As from Fig.5.49, the volume fraction seems to remain constant. This could be due to a very slow shrinking.
- 4. Pressure. As from Fig.5.50, in accordance with the pressure, all mixtures allow to the pressure to reach a constant value.

Regarding the behavior of the region 14, during shrinking:

- 1. Radius. As from Fig.5.51, the more the silicates comprise the porous media, the more the region exhibits higher averaged radius. This means that the region has better chances to be predominated by porous media, if more silicates are inserted.
- 2. Velocity. As from Fig.5.52, although the velocity seems to be very slow, highest kinetics are enhanced by a porous media, reach in carbonates. Due to their lower stiffness, they allow more compenetration of particle of the caprock.
- 3. Volume Fraction. As from Fig.5.53, the volume fraction seems to remain constant. This could be due to a very slow shrinking.
- 4. Pressure. As from Fig.5.54, in accordance with the pressure, all mixtures allow to the pressure to reach a constant value.

Regarding the behavior of the region 23, during shrinking:

1. As from fig.5.55, the averaged radius presents a small fluctuation in the most carbonatereach porous media. In the other compositions, it seems to remain constant

- 2. As from fig.5.56 The velocity is always close to the zero, although slight starting value is happening with higher silicates percentage.
- 3. As from fig.5.57 The volume fraction is constant, apart from the small fluctuations in the carbonate-rich cases
- 4. As from fig.5.58 The pressure as a constant value, which is higher if more silicates are comprised in the porous media


Figure 5.3: Energy ratio in sample preparation. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.4: Coordination number during sample preparation. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.5: Stress during sample preparation. The zz- hydrostatic component is represented. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.6: Deviatoric stress during sample preparation. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.7: Averaged radii in Region 5 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted lines mean phases I until III. (Source: the Author).



Figure 5.8: Averaged velocities in Region 5 during sample preparation. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line mean phases I until III. (Source: the Author).



Figure 5.9: Averaged volume fraction in Region 5 during sample preparation. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted lines mean phases I until III. (Source: the Author).



Figure 5.10: Averaged Pressure in Region 5 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line mean phases I until III. (Source: the Author).



Figure 5.11: Averaged Radius in Region 14 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.12: Averaged Velocity in Region 14 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.13: Averaged Volume Fraction in Region 14 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.14: Averaged Pressure in Region 14 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.15: Averaged Radius in Region 23 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.16: Averaged Velocity in Region 23 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.17: Averaged Volume Fraction in Region 23 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.18: Averaged Pressure in Region 23 during sample preparations. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.19: Energy ratio during testing. Box side = 0.3 m, Lithostatic load equal to 10³ Pa, The dissolution applied with two t.frequencies 10⁻¹⁵ and 10⁻¹⁷, respectively. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.20: Coordination Number during testing. Box side = 0.3 m, Lithostatic load equal to 10^3 Pa, The dissolution applied with two t.frequencies 10^{-15} and 10^{-17} , respectively. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.21: ZZ-component of the stress in a sample during testing. Box side = 0.3 m, Lithostatic load equal to 10³ Pa, The dissolution applied with two t.frequencies 10⁻¹⁵ and 10⁻¹⁷, respectively. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.22: Deviatoric stress during testing. Box side = 0.3 m, Lithostatic load equal to 10³ Pa, The dissolution applied with two t.frequencies 10⁻¹⁵ and 10⁻¹⁷, respectively. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.23: Energy ratio during testing. Box side = 0.3 m, Lithostatic load equal to 10³ Pa, The dissolution applied with two t.frequencies 10⁻¹⁶ and 10⁻¹⁸, respectively. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.24: Coordination Number during testing. Box side = 0.3 m, Lithostatic load equal to 10³
Pa, The dissolution applied with two t.frequencies 10⁻¹⁶ and 10⁻¹⁸, respectively. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.25: ZZ-component of the stress during testing. Box side = 0.3 m, Lithostatic load equal to 10³ Pa, The dissolution applied with two t.frequencies 10⁻¹⁶ and 10⁻¹⁸, respectively. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.26: Deviatoric stress during testing. Box side = 0.3 m, Lithostatic load equal to 10³ Pa, The dissolution applied with two t.frequencies 10⁻¹⁶ and 10⁻¹⁸, respectively. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.27: Energy ratio during accelerated unlimited shrinking. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.28: Coordination Number during accelerated unlimited shrinking. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.29: Stress during accelerated unlimited shrinking. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.30: Deviatoric stress during accelerated unlimited shrinking. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.31: Averaged radius in Region 5, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.32: Averaged velocity in Region 5, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.33: Averaged volume fraction in Region 5, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.34: Averaged pressure in Region 5, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.35: Averaged radii in Region 14, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.36: Averaged velocity in Region 14, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.37: Averaged volume fraction in Region 14, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.38: Averaged pressure in Region 14, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).


Figure 5.39: Averaged radius in Region 23, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.40: Averaged velocity in Region 23, during accelerated unlimited shrinking. Colored lines indicates mixtures in the porous media, continuousdashed colored lines indicates bulks, vertical black dotted line stand for phases I until III.(Source: the Author).



Figure 5.41: Averaged pressure in Region 23, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.42: Averaged pressure in Region 23, during accelerated unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.43: Energy ratio in scaled unlimited shrinking. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.44: Coordination number in scaled unlimited shrinking. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).





Figure 5.45: Stress in scaled unlimited shrinking. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.46: Deviatoric stress in scaled unlimited shrinking. Colored lines represent output quantities in regions. Dotted vertical lines represent simulation phases, in order: insertion, relax, loading, dissolution. (Source:the Author).



Figure 5.47: Averaged Radius in Region 5, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuousdashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.48: Averaged Velocity in Region 5, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuousdashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.49: Averaged Volume Fraction in Region 5, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.50: Averaged Pressure in Region 5, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.51: Averaged Radius in Region 14, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuousdashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.52: Averaged Velocity in Region 14, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.53: Averaged Volume Fraction in Region 14, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.54: Averaged Pressure in Region 14, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.55: Averaged Radius in Region 23, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuousdashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.56: Averaged Velocity in Region 23, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.57: Averaged Volume Fraction in Region 23, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).



Figure 5.58: Averaged Pressure in Region 23, during scaled unlimited shrinking. Colored lines indicates different mixtures in the porous media, continuous-dashed colored lines indicates two bulks, while vertical black dotted line stand for phases I until III. (Source: the Author).

Chapter 6

Conclusions and recommendations

6.1 Conclusion

The present research showed that the discrete element method, introduced by Cundall and Strack [7], can be applied within the discipline of carbon capture and storage and more specifically, for geological storage of CO_2 purposes. DEM can give insights regarding the micro-mechanisms taking place in a geological reservoir under CO_2 storage conditions. It was possible with DEM, to model a representative element of volume (REV), as delineative of a geological reservoir that undergoes in-situ mineral dissolution, that is likely to enhanced by the stored CO_2 , while being subjected to the weight of the above-standing soil. This latter perturbation is called lithostatic stress.

6.1.1 Methodology

The research firstly established a DEM-based methodology and applied it to a simplified REV. In a transition from the real reservoir to its numerical representation, the following assumptions were established.



Figure 6.1: Schematic representation of the establish methodology (Source: the Author).

1. Storage-phase related. It was assumed that the geological reservoir is currently storing CO₂ in a phase that is far from its first and only injection. The water present in the geological formation was assumed to be CO₂ saturated but still able to activate in-situ mineral dissolution. The mixing between the formation water and the injected CO_2 was considered slow. It was also assumed that an idealized mixture comprehensive of injected CO_2 and formation water can chemically react faster than their trend of diffusion within in-situ pores. In other words, the diffusion of the fluid mixture in the pores, is negligible compared to their chemical effect, within the reservoir.

- 2. Solid-phase related. It was assumed that the in-situ grains are discrete, spherical and smooth particles of which the average radius is assumed to be known. Then, each spherical particle, was seen as an homogeneous compound representing the most reactive minerals one could find in in-situ grains. Since the Earth's crust is mainly comprised of silicates and carbonates, representative compounds belonging to this mineral families were considered. This research considered pure silica and feldspars as representative of the first, while calcite for the second mineral family.
- 3. Fluid-phase related. The fluid was modeled as an idealized mixture of formation water and supercritical CO₂ and it was of interest not to study the consequences after the immediate activation of the dissolution process that can be enhanced by the CO₂. In a conceptual summation of storage- and fluid- related assumption, the fluid was modeled in a implicit manner. Its physical composition was not included in the simulation but its chemical effect on the grains is modeled instead.
- 4. System-phase related. It was first assumed that all pores of the reservoirs are filled with an idealized mixture of supercritical CO₂ and formation water. This was followed by the assumption of temperature being constant over time and geological reservoir being subjected to only two major perturbations, namely mineral dissolution and the stress deriving from the weight of the above-standing soil, which is called lithostatic load.

A simplified geological domain was therefore, defined. At this point, a representative element of volume (REV) of such a domain was studied instead of its entirety. By means of DEM it is possible to first compute microscopic quantities, derived from contact interactions, that can be averaged in order to have an understanding of the macroscopic behavior of the bulk. These quantities served the purpose of qualitatively study the trends of bearing capacity inside the REV.

It was noted that within DEM, it is not possible to create a REV and apply a chemicalgeotechnical perturbation, making use of only one simulation phase. Therefore, a multistaged simulation that takes the sequentiality of the phenomena into account, is needed. In a first instance, the REV needs to be numerically prepared, which was possible through the above-mentioned assumptions. Secondly, the REV needed to be physically prepared to recreate the stress condition typical of the site. Thirdly, the chemical effect was applied. Going into more details, the research has established the following phases, that can be staged by means of the above-mentioned averaged quantities, namely:

1. Insertion phase

- 2. Relaxation phase
- 3. Loading phase
- 4. Shrinking phase

Each phase has been intrinsic of novelty. In the insertion phase the simulation domain needs to be created and particles inserted. When creating the simulation domain, it was possible to design a separator-wall that kept particles of two different regions, perfectly separated. This division was created by defining a double-layered wall, with an empty region in between where particles are not allowed to be created. It was observed that this division can be controlled by means of the ratio between kinetic and potential energy. When this quantity is stably equal or lower than 10^{-6} , particles contained in each region presented such a low kinetic that they two particles laid one on top of each other, stably, without mixing with the other specie. This has been an improvement compared to the traditional DEM approaches, which involves the usage of two separate domain. It was understood that by using such a domain, one study interface-related problems by using only one simulation setup.

The influence of the mineralogy was modeled as a variable mixture in weight of the particles representing minerals in the porous media. Representative minerals were considered, namely silica (SiO₂) and CaO (SiO₂). Five mixtures were adopted, ranging from a porous media completely comprised of carbonates (100% SiO₂ vs. 0% CaO), of only silicates (0% SiO₂ vs. 100% CaO) or of three possible mixtures of the two (i.e. 25% SiO₂ vs. 75% CaO, 50% SiO₂ vs. 50% CaO, 75%, SiO₂ vs. 25% CaO)

In the presented methodology, several real values were adopted. This applied for Young's Modulus, Poisson ratio, coefficient of restitution. The cohesion energy density was assumed, due to a lack of literature within its ranges in geological science. Radius of the same order of magnitude were adopted.

After several attempts, the initial volume fraction was set equal to 0.62 for each region. This value was able to return a stably solid and isotropic REV, with internal stress condition inferior to the desired lithostatic load. In this phase gravity was not applied. When particles are inserted, an overlap is present which fuses repulsion, therefore, kinetics.

In a third phase a typical lithostatic load can be applied, in the present research 10⁷ Pa has been selected. In this research, the concept of the lithostatic load has been from a continuum perspective to a more discrete one. Traditionally, the lithostatic load can be estimated by assuming a typical soil weight and knowing the depth. Nevertheless, this vision does not take into account grain interactions. In the present research, the lithostatic load has been converted into a resultant force acting on the grain, which an approach that better copes with the discreteness of soils.

This phase can be staged by means of stress. Firstly, after the sample has undergone relaxation one should always observe the internal stress condition of the sample. In order for the research to continue, the internal stress condition after relaxation, needs to be inferior to the lithostatic load one wants to apply. Subsequently, one should load the REV, until a

stably constant value of stress is reached. When this step was achieved, the sample was considered prepare and ready for being subjected to dissolution.

In a fourth phase, since the fluid has not been modeled explicitly, its chemical effect on the grains has been modeled has spherical particles, shrinking in radius. This representation needs some assumptions and has offered some advantages.

It has been possible to apply a relatively simple model, that can be linked to real experiments. This can happened under the assumption of spherical particle at constant density.

Subsequently, the methodology, has first converted the trend of the mass loss due to dissolution, into radius loss. Then, one can decide if the model needs to take into account the limit imposed by fluid saturation, or not. The unlimited shrinking model might sound not consistent to many chemistry-oriented scientist, but it is of added value for geo-structure-related practitioners, as it can reveal if collapse can take place.

Once the initial and final radius is known, one needs to define the trend, in order to know how fast the final condition is reached. Thirdly, a peculiarity of this research is the possibility of implementing how often the dissolution takes place. This can be expressed in terms of turnover frequency, which is a spillover from the pharmaceutical industry. In real experiments, this quantity defines with precision, how frequently, any solute immersed in a solvent loses mass. Nevertheless, this research did not run simulations which last as real experiments. Therefore, the experimental values can be first calculated, then the value can be scaled down (since the simulations are shorter) depending on the length of the simulation.

During this phase it was important two distinguish between two types of averaged quantities, namely bulk- and per-cell- quantities. In DEM simulations one can define a spatial region where particles can be inserted, which is likely to remain the same for the whole simulation. These types of regions are called "static" regions. At the same time, spherical particles were marked as belonging to a specific material type, at the beginning of the simulation. As it is possible that particles can move from a region to another, e.g. by means of the load, the stress for particles belonging to a type is constantly calculated, but it is averaged over the initial region, which is not the volume of reference anymore. To cope with this problem, the concept of per-cell- quantities was introduced. The software LIGGGHTS was let free to divide the simulation domain into smaller cells, by inputting a cutoff. The smallest cutoff possible, equal to 3, was selected since it return the highest number of cells.

Definitely, the established DEM methodology can be adopted either within the monitoring of a reservoir, and during the reservoir selection process.

6.1.2 Failure analysis

The research question formulated in Section 1.1.1: *Can mineral dissolution in the long-term geological storage, affect the sealing capacity of the geological formation, under a geotechnical perspective?* can be answered positively. Indeed, the mineral dissolution that can characterize the geological reservoir in the long-term, can arm the reservoir even at low frequencies. The present work has shown that even a very small reduction in volume over time, might results in local collapses.

The following conclusion regarding the *material properties* can be listed:

- 1. The research has observed that either the stiffness of the in-situ grains in combination also influence the bearing capacity during dissolution
- 2. The cohesion between grains did not seem to attain the caprock failures

The following conclusion regarding the *chemical properties* can be listed:

- 1. Practitioners should known how frequently a typical grain can get dissolved when injecting CO₂. This advice does not seem to be mentioned by the IPCC [1]
- An instantaneous volume reduction can cause a sudden change in the bearing capacity

The following conclusion regarding the the novelty of the research can be listed:

- 1. having a qualitative estimate of how the stress situation can change due to the dissolution
- understanding instantaneous micro-mechanisms fused by the in-situ mineral dissolution

Although assumptions were needed in order to conduct the DEM simulations, this research has shown a typical mechanism, which can be visualized in Fig.6.2:

In Fig.6.2, it is depicted that, under geological storage condition, if CO₂ is injected, attention must be paid to the solubility of the in-situ mineral. If grains dissolve, contact between grain can lack, leading to an enhanced kinetic. At this point, it the grain that can get dissolved is relatively stiff, bearing capacity can be saved. If not bearing capacity can be loss. These understanding should be spread around practitioners of geological storage, with great enthusiasm as:

- 1. One can not only use these insights in the monitoring phase, but also in the sitecharacterization phase
- 2. While, a traditional approach to understand these mechanisms, is more expensive, as it would have required drilling and/or lab testing, with subsequent use of laboratory equipped in such a way that they can recreate supercritical fluid conditions, this research methodology has proven to be economically-feasible.

In this research, homogeneous and spherical particles are considered. This means that, the more a geological reservoir can be characterized by high grain sphericity, with high homogeneity, the more DEM gets a bit closer to reality. In addition, one should consider that the research has been conducted by means of building a representative element of volume of an idealized reservoir. It should be remembered that, in contrary with the finite element method, discrete element method, can receive real material property as input and can describe the real physics (of contacts) between grains.



Figure 6.2: Proposed typical micro-mechanisms during in-situ mineral dissolution

With discrete element method, it is possible to look at the microscopic level of a geological reservoir. Subsequently, by means of averaging, it is possible to obtain bulk characteristics. There is more, with DEM simulations, particle and averaged information can be accessed at any time-step, and the same script which could be written for one analysis, could be reused in other cases.

Within these research, local collapse of the porous media, has shown to be possible. Four isotropic indicator have been used to identify the collapse of a sample: coordination number, stress tensor, deviatoric stress and the ratio between kinetic and potential energy. All of them together are needed to understand if there is collapse. In all simulations conducted within the research, a double-layer has been adopted. Every setup revealed that, whenever one of the isotropic quantities changes in the porous media, this affects the correspondent quantity in the cap rock.

Even at lithostatic loads lower that the one obtained from IPCC's [1] recommendations, it is understood that the mineralogy should be also considered, especially when designing a reservoir. Simulations have shown that when carbonatic grains then to be predominant in the porous media, if dissolution takes, place, the grains tent to loose contact in a relatively sharper fashion. Accordingly, if the porous media can be defined as mainly carbonatic, simulations have shown that a relatively lower stress condition can be reached, in the stress

tensor. No matter if the porous media is mostly made carbonatic or silica-rich, when the dissolution, modeled as shrinking particles, was applied, the ratio between the kinetic and potential energy, was always raising. Therefore, it is possible that dissolution can induct new kinetics in the reservoirs, which imply a loss in the potential energy, which means a loss of contacts between grains.

It might seem that using a not-controlled dissolution model (shrinking core model), is unrealistic. Instead this model can cope with the fact that in a geological reservoir, new injection could be made over time, which means reactivation of the dissolution, as the new fluid is not saturated. In this sense, it can help practitioner in understanding how the structure of the reservoir behaves in the long-term. This research has proven that several optimizations can be conducted within discrete element method applied to geological storage of CO₂ and soil engineering. While DEM simulations are often conducted with one sample (of any shape), containing one mixture of material, in the present work, one sample has been divided in two layers. This procedure can be adopted for simulating any type of interfacing layers within soil engineering, instead of simulating them in separate simulations.

6.2 Recommendations

In this section, a list of major recommendations for improving the established DEM methodology and its interpretation is presented.

Firstly, an extended parametric study can be conducted reusing the same methodology established in this paper. In an approach relatively close to Monte-Carlo simulations, a new research can be conducted reusing the same methodology and tools. In this case, one could use the present scripts and define every parameter of interest as a variable that can range from a minimum to a maximum value, defining a cutoff in between. Nevertheless, since several parameters are involved in DEM simulations, it is highly recommended to change one at the time.

Different samples can be created, changing the following parameters.

- Other Young's Modulus and Poisson ratio values can be used as input. Although carbonates and silicates are the most recurrent minerals in the Earth's crust, soils are complex mixtures that involves other mineral families. In the present research, a specific set of microscopic parameters has been selected, but either practitioner and academics are encouraged to repeat the research with different values. For the Young's Modulus, any value between 10⁶ Pa and 10¹² can be set as input.
- 2. The Poisson ratio can be set according to the level of particle (an-)isotropy.
- 3. With regards to friction, if spherical particles are of interest, a different coefficient could be adopted. In case of using non-spherical particle and, hopefully, real (random) shapes showed by real grains, one should bear in mind that the friction would not pop up in terms of coefficient by will pop up from the grain-grain interlocking.

- 4. Coefficient of restitution. Firstly, the coefficients of restitution adopted in the present research was considered constant over time. If needed, the implementation of a variable coefficient of restitution can provide more precise insights within DEM simulations. Secondly, the coefficient of restitution can be obtained from experiments or real sampling. It is highly recommended to repeat the research inserting different values, since collision within different soils might dissipate energy in a more diverse trend.
- 5. Cohesion energy density. The cohesion energy density is a theoretical value that describes cohesion, typically between two atoms. It is possible to define the cohesion energy density for grains, but little research has been conducted so far. Cohesion energy density can be calculated mostly from molecular dynamics simulation. If new insights regarding cohesion energy density of soil grains might be discovered, it is highly recommended to include them in the present research.
- 6. Volume fraction. The initial volume fraction of this study was set to 0.62, but different values can be used as soils exhibits various porosities. A recommendation is to repeat the present research inserting different initial volume fractions. In this case, one should pay attention to the number of atoms created. On the one hand, by inserting a too low volume fraction, one might obtain a sample that does not represent a solid (stress close to zero and coordination number less than 4 can help the monitoring). On the other hand, choosing a higher volume fraction, means higher stress situation after the sample relaxation. In this case, one would have to redefine the lithostatic load of interest accordingly.
- 7. Radius. In this research radii belonging to the same order of magnitude were selected. In addition, grain modeled the relevant minerals which can get dissolve in the reservoir. A recommendation is to repeat the present research using different radius distributions, to cover a wider spectrum of grains that can be modeled.
- 8. Density. In this research particle density was considered equal to 2700 kg/m³ and constant. One can repeat the present research implementing a more accurate density value. It is true that real grains often change density when they get subjected to dissolution. Nevertheless, if particle density would be implemented as variable over time, it should the either the unlimited and limited shrinking particle model hereby adopted are not applicable anymore.

The sample can be prepared in a different manner.

In this research, a constant and instantaneously applied load was adopted to simulate an initially-fast process of sedimentation. While this choice has been selected since it is the worst case scenario, there are other two procedures which can model the same process. The first involves the usage of a "stress-controlled" wall (sometimes called "pressurecontrolled wall"). This tool consists of a mesh (representing a real element of wall), which is used within DEM simulation to compress a sample until a target stress (pressure) is achieved. This tool best fits the modeling of relatively slow compression and sedimentation, but it can also be used to model fast compression.

The modeling of the dissolution, can be extended.

As technology and science progress, new experiments regarding dissolution of mineral in supercritical fluids might be discovered. This can create new insight for the established DEM methodology in terms of limit, turnover frequency and trend of dissolution.

- 1. Limit. If new kinetic rate constants regarding mineral dissolution in supercritical fluids, these can be implemented in the present methodology.
- Turnover frequency. As in the previous point new kinetic rate constants might be implemented to have insights regarding dissolution. In addition, there is need for a model able to describe the change in size of the reactive surface area, at least for the most relevant minerals.
- 3. Trend of dissolution. In the present research a negative exponential trend was adopted, in the ratio between diffusivity and speed of chemical reaction within geological storage of CO₂ has not been fully understood yet. On the one hand, if one would like to model geological reservoir where the fluid is characterized by high diffusion and slow chemical reaction, one could implement a reaction-limited model, assuming that the reaction at the solid-liquid interface is controlling the rate of dissolution. If the opposite occurs, one can implement a model with dissolution limited by diffusion.
- 4. Saturation. The so-called limited shrinking could be implemented, allowing to simulate dissolution bounded by fluid saturation.

The fluid can be explicitly modeled.

In the present research the fluid was not modeled, but its chemical effect was instead. It is known that DEM modeling of fluid is extremely complex and computationally expensive, but it could make the modeling more realistic. Therefore, a recommendation for DEM experts is to redo the presented research, including the physical molecule of the fluid.

Extension of the simulation to other domains outside the interface.

In general, the present methodology can be adopted for modeling REV of idealized reservoirs, not necessarily belonging to the interface between the caprock and the porous media. This, would also allow the inclusion of diverse lithostatic loads.

improved localized quantities, more coarse-graining.

The established methodology can qualitatively determine the occurrence of collapse in a geological reservoir, in particular of the caprock due to the dissolution of the porous media being dissolved by means of supercritical CO₂. In LIGGGHTS, it was not possible to define a region able to follow the particles of a specific material, when they were moving inside the

REV. This means that only "static" regions are implemented in LIGGGHTS and there is no "dynamic" region. Not having such a type of region can created imprecisions, especially in the calculation of stress in the bulk. Therefore, the stress acting on a group of particles is averaged over a region that is not 100% correct. In quasi-static simulations, such as in this research, results are not deviating so much. In case one would conduct simulations which are more dynamic, the deviation is wider.

This was why quantities averaged in the bulk are accompanied by per-cell averaging. The present research has referred to quantity averaging, of three regions, but if one could extend this evaluation to the totality of the cell, which would improve quality and quantity of the coarse-graining point of the present work.

Once this improvement is conducted, there would be more information to define how the collapse occurs. Therefore, failure criteria can be applied. In particular, the recommendation is to start with the Mohr-Coulomb failure criterion, to evaluate the shear stress of the REV. The present work has already calculated the quantity need by the criterion.

Ideally, this procedure can be conducted for as many parameters as desired. On a more practical level, one needs to take care of the storage memory occupied by each simulation (in this research the averaged occupied size is circa 2 gigabyte per simulation, but it is possible to write a script in C++ or matlab that can help forecasting the storage memory needed).

Bibliography

- S. Benson, P. Cook, J. Anderson, S. Bachu, H. Nimir, B. Basu, J. Bradshaw, G. Deguchi, J. Gale, G. von Goerne *et al.*, "Underground geological storage," *IPCC special report on carbon dioxide capture and storage*, pp. 195–276, 2005.
- [2] R. E. Sims, H.-H. Rogner, and K. Gregory, "Carbon emission and mitigation cost comparisons between fossil fuel, nuclear and renewable energy resources for electricity generation," *Energy policy*, vol. 31, no. 13, pp. 1315–1326, 2003.
- [3] H. Barten, "International energy agency," 2005.
- [4] B. Metz, *Carbon dioxide capture and storage: special report of the intergovernmental panel on climate change.* Cambridge University Press, 2005.
- [5] P. J. Vergragt, N. Markusson, and H. Karlsson, "Carbon capture and storage, bioenergy with carbon capture and storage, and the escape from the fossil-fuel lock-in," *Global Environmental Change*, vol. 21, no. 2, pp. 282–292, 2011.
- [6] N. Kampman, M. Bickle, M. Wigley, and B. Dubacq, "Fluid flow and co 2–fluid–mineral interactions during co 2-storage in sedimentary basins," *Chemical Geology*, vol. 369, pp. 22–50, 2014.
- [7] P. A. Cundall and O. D. Strack, "A discrete numerical model for granular assemblies," *Geotechnique*, vol. 29, no. 1, pp. 47–65, 1979.
- [8] R. S. Haszeldine, "Carbon capture and storage: how green can black be?" Science, vol. 325, no. 5948, pp. 1647–1652, 2009.
- [9] M. Petro, "Experimental study of rock-fluid interaction using automated multichannel system operated under conditions of co2-based geothermal systems," in 38th Annual Workshop on Geothermal Reservoir Engineering, Stanford, CA, Feb. 11-13, 2013, 2014.
- [10] S. H. S. R. C. W. J. M. E. F. J. P. G. S. J. T. B. Chadwick, A. ; Holloway, "External review of the storage plan for the peterhead carbon capture and storage project." *British Geological Survey*, vol. 1, no. 1, pp. 1–22, 2014.
- [11] C. Azar, K. Lindgren, M. Obersteiner, K. Riahi, D. P. van Vuuren, K. M. G. den Elzen, K. Möllersten, and E. D. Larson, "The feasibility of low co2 concentration targets and

the role of bio-energy with carbon capture and storage (beccs)," *Climatic Change*, vol. 100, no. 1, pp. 195–202, 2010.

- [12] Y. Okuyama, N. Todaka, M. Sasaki, S. Ajima, and C. Akasaka, "Reactive transport simulation study of geochemical co 2 trapping on the tokyo bay model-with focus on the behavior of dawsonite," *Applied geochemistry*, vol. 30, pp. 57–66, 2013.
- [13] W. Stumm et al., Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems. John Wiley & Son Inc., 1992.
- [14] S. K. Sinha and B. J. Briscoe, *Polymer tribology*. World Scientific, 2009, vol. 697.
- [15] A. Islam, A. Y. Sun, and C. Yang, "Reactive transport modeling of the enhancement of density-driven co2 convective mixing in carbonate aquifers and its potential implication on geological carbon sequestration," *Scientific reports*, vol. 6, 2016.
- [16] M. A. Winters, P. G. Debenedetti, J. Carey, H. G. Sparks, S. U. Sane, and T. M. Przybycien, "Long-term and high-temperature storage of supercritically-processed microparticulate protein powders," *Pharmaceutical research*, vol. 14, no. 10, pp. 1370–1378, 1997.
- [17] N. Budisa and D. Schulze-Makuch, "Supercritical carbon dioxide and its potential as a life-sustaining solvent in a planetary environment," *Life*, vol. 4, no. 3, pp. 331–340, 2014.
- [18] M. Raventós, S. Duarte, and R. Alarcón, "Application and possibilities of supercritical co2 extraction in food processing industry: an overview," *Food Science and Technology International*, vol. 8, no. 5, pp. 269–284, 2002.
- [19] J. P. Kaszuba, D. R. Janecky, and M. G. Snow, "Experimental evaluation of mixed fluid reactions between supercritical carbon dioxide and nacl brine: Relevance to the integrity of a geologic carbon repository," *Chemical Geology*, vol. 217, no. 3, pp. 277–293, 2005.
- [20] L. André, M. Azaroual, and A. Menjoz, "Numerical simulations of the thermal impact of supercritical co2 injection on chemical reactivity in a carbonate saline reservoir," *Transport in porous media*, vol. 82, no. 1, pp. 247–274, 2010.
- [21] B. Das and K. Sobhan, *Principles of geotechnical engineering*. Cengage Learning, 2013.
- [22] R. Lancellotta, *Geotechnical engineering*. CRC Press, 2008.
- [23] S. Luding, "Introduction to discrete element methods: basic of contact force models and how to perform the micro-macro transition to continuum theory," *European Journal* of Environmental and Civil Engineering, vol. 12, no. 7-8, pp. 785–826, 2008.

- [24] E. S. Oran and J. P. Boris, *Numerical simulation of reactive flow*. Cambridge University Press, 2005.
- [25] G. Guthrie, J. W. Carey, D. Bergfeld, D. Byler, S. Chipera, H.-J. Ziock, and K. Lackner, "Geochemical aspects of the carbonation of magnesium silicates in an aqueous medium," in *NETL Conference on Carbon Sequestration*, 2001, pp. 1–14.
- [26] Y.-Q. Shang, S.-T. Wang, and H.-W. Chen, "The principle of discrete element method and its application in the study of regional tectonic stability," *Acta Seismologica Sinica*, vol. 6, no. 2, pp. 389–395, 1993.
- [27] E. Catalano, "Infiltration effects on a partially saturated slope-an application of the discrete element method and its implementation in the open-source software yade," Ph.D. dissertation, Master thesis at UJF-Grenoble, 2008.
- [28] A. Bottero, R. Negre, J. Pastor, and S. Turgeman, "Finite element method and limit analysis theory for soil mechanics problems," *Computer Methods in Applied Mechanics and Engineering*, vol. 22, no. 1, pp. 131–149, 1980.
- [29] J. Anthonis and H. Ramon, "Comparison between the discrete and finite element methods for modelling an agricultural spray boomâĂŤpart 2: automatic procedure for transforming the equations of motion from force to displacement input and validation," *Journal of sound and vibration*, vol. 266, no. 3, pp. 535–552, 2003.
- [30] S. Luding, "Particulate solids modeling with discrete element methods," CHoPS-05 CD proceedings, pp. 1–10, 2006.
- [31] H. Kruggel-Emden, M. Sturm, S. Wirtz, and V. Scherer, "Selection of an appropriate time integration scheme for the discrete element method (dem)," *Computers & Chemical Engineering*, vol. 32, no. 10, pp. 2263–2279, 2008.
- [32] K. Johnson, "One hundred years of hertz contact," Proceedings of the Institution of Mechanical Engineers, vol. 196, no. 1, pp. 363–378, 1982.
- [33] K. L. Johnson and K. L. Johnson, *Contact mechanics*. Cambridge university press, 1987.
- [34] E. Dintwa, E. Tijskens, and H. Ramon, "On the accuracy of the hertz model to describe the normal contact of soft elastic spheres," *Granular Matter*, vol. 10, no. 3, pp. 209–221, 2008.
- [35] E. Barthel, "Adhesive elastic contacts: Jkr and more," *Journal of Physics D: Applied Physics*, vol. 41, no. 16, p. 163001, 2008.
- [36] J. Marshall, "Discrete-element modeling of particulate aerosol flows," *Journal of Computational Physics*, vol. 228, no. 5, pp. 1541–1561, 2009.

- [37] K. Johnson, K. Kendall, and A. Roberts, "Surface energy and the contact of elastic solids," in *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, vol. 324, no. 1558. The Royal Society, 1971, pp. 301–313.
- [38] C. Kloss and C. Goniva, "Liggghts-open source discrete element simulations of granular materials based on lammps," *Supplemental Proceedings: Materials Fabrication, Properties, Characterization, and Modeling, Volume 2*, pp. 781–788, 2011.
- [39] —, "Liggghts: a new open source discrete element simulation software," in *Proceed-ings of The Fifth International Conference on Discrete Element Methods, London, UK*, 2010, pp. 25–26.
- [40] R. Gupta, "General physics motivations for numerical simulations of quantum field theory," *Parallel Computing*, vol. 25, no. 10, pp. 1199–1215, 1999.
- [41] J. H. Ferziger and M. Peric, Computational methods for fluid dynamics. Springer Science & Business Media, 2012.
- [42] A. Thornton, D. Krijgsman, A. Voortwis, V. Ogarko, S. Luding, R. Fransen, S. Gonzalez, O. Bokhove, O. Imole, and T. Weinhart, "A review of recent work on the discrete particle method at the university of twente: An introduction to the open-source package mercurydpm," 2013.
- [43] R. Hill, "Elastic properties of reinforced solids: some theoretical principles," *Journal of the Mechanics and Physics of Solids*, vol. 11, no. 5, pp. 357–372, 1963.
- [44] A. Singh, V. Magnanimo, K. Saitoh, and S. Luding, "The role of gravity or pressure and contact stiffness in granular rheology," *New journal of physics*, vol. 17, no. 4, p. 043028, 2015.
- [45] C. I. Steefel and A. C. Lasaga, "A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems," *American Journal of science*, vol. 294, no. 5, pp. 529–592, 1994.
- [46] C. Saline Aquifer, "The solubility of supercritical co2 into pure water and synthetic utsira porewater."
- [47] J. W. Tester, W. G. Worley, B. A. Robinson, C. O. Grigsby, and J. L. Feerer, "Correlating quartz dissolution kinetics in pure water from 25 to 625 c," *Geochimica et Cosmochimica Acta*, vol. 58, no. 11, pp. 2407–2420, 1994.
- [48] U. Svensson and W. Dreybrodt, "Dissolution kinetics of natural calcite minerals in co 2-water systems approaching calcite equilibrium," *Chemical Geology*, vol. 100, no. 1, pp. 129–145, 1992.
- [49] A. E. Blum and L. L. Stillings, "Feldspar dissolution kinetics," *Reviews in Mineralogy and Geochemistry*, vol. 31, no. 1, pp. 291–351, 1995.

[50] K. Nagy, "Dissolution and precipitation kinetics of sheet silicates," *Reviews in Mineral*ogy and Geochemistry, vol. 31, no. 1, pp. 173–233, 1995.

Appendix: Coding

In this section of the appendix the relevant script that has been developed during the research are reported.

Script in LIGGGHTS: "LoaderInfiniteDissolver"

This script, written for LIGGGHTS-PUBLIC v.3.3.1, creates two layers, then inserts particles with specific material properties in each. The code applies sample preparation and perturbation described in Section. 4. The peculiarity of this code are

- Its capability of generating two layers in one box (no need for merging multiple simulations)
- 2. Loading a packing by means of instantaneous loading
- 3. Loading and shrinking particles, which might be very useful for simulation of many chemical-industrial processes
- 4. The shrinking is "limited" (aka the particles will have a limiting radius, or threshold)

For consultancy of for the full version please email the Author (pecorielloluca@gmail.com)

```
variable InitialVolumeFraction equal 0.62
variable Percentage Pm Type2 equal 0.5
variable Percentage_Pm_Type4 equal 0.5
variable k_0_type2 equal 1e-15
variable k_0_type4 equal 1e-17
variable DumpRonny equal 1000
variable Dissolve_tp2_every equal
                                  1
variable Dissolve_tp4_every equal
                                    1
include INCLUDED/0_PRELIMINARIES
include INCLUDED/5_SELECTED_TIMESTEP
include INCLUDED/0_VARIABLES
include INCLUDED/1_MATERIAL_PARAMETERS_AS_VARIABLES
include INCLUDED/2_TIMING
include INCLUDED/3_REGION
#read_restart Sample/Recovery_PTS2_ &
    ${Percentage_Pm_Type2}_PTS4_${Percentage_Pm_Type4}_29000000.restart
create box 4 Box
neighbor 0.065 bin
neigh_modify every 2 delay 0 check yes page 100000
include INCLUDED/4_PARTICLE_PROPERTIES
```
```
include INCLUDED/5 SELECTED TIMESTEP
include INCLUDED/6_CONTACT_MODEL
include INCLUDED/8_WALLS_RESTART
include INCLUDED/9_INITIAL_GROUPIEZ
fix ts_check all check/timestep/gran 1000 0.1 0.1
fix Spherical_Integration all nve/sphere
fix BackGroundViscosity
                            all viscous 0.1
include INCLUDED/11_LOCAL
compute Initial_overlap_approx all reduce ave c_local1[32]
variable Max_Approximated_Overlap equal c_Initial_overlap_approx
include INCLUDED/12_RESET_TIMESTEP_RESTART
fix Ave_Euler all ave/euler nevery ${DumpRonny} cell_size_relative 3 parallel no
include INCLUDED/0 VARIABLES
include INCLUDED/13_GROUPIEZ
include INCLUDED/14_KINETIC_ENERGIES
include INCLUDED/15_POTENTIAL_ENERGIES
include INCLUDED/16_ENERGY_CHECKS
include INCLUDED/17_TOTAL_ENERGY
include INCLUDED/18 CONTACTS
include INCLUDED/19_VOLUME_FRACTION
include INCLUDED/20_STRESS
compute All_Radii_Type2 Type2 property/atom radius
compute All_Radii_Type4 Type4 property/atom radius
compute Sum_Radius_Type2 all reduce sum c_All_Radii_Type2
compute Sum_Radius_Type4 all reduce sum c_All_Radii_Type4
variable Radii_Type2 equal c_Sum_Radius_Type2/count(Type2)
variable Radii_Type4 equal c_Sum_Radius_Type4/count(Type4)
## LOAD
include INCLUDED/SUPERMASSIVE_BLACK_LOAD
## Activate dissolution LIMITED - MODE
include INCLUDED/ACTIVATE_DISSOLUTION_LIMITED
thermo_style custom step dt time atoms
thermo ${DumpRonny}
thermo_modify lost ignore norm no
compute_modify thermo_temp dynamic yes
run ${elongate5}
```