

Petroleum and Mining Engineering

Master of Science Thesis

A Review of Studies on Reservoir Responses during CO2, H2, and N2 Storage.

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Abstract

This thesis presents a literature review on underground gas storage in rock formations, with a specific focus on CO_2 geological storage. The review highlights the intricate interactions between CO_2 and reservoir rocks, caprocks, and clay minerals, emphasizing the complexity involved in predicting and optimizing the performance of CO_2 storage projects.

The impact of CO_2 on rock strength and mechanical properties is a key aspect discussed in the review. Studies demonstrate that CO_2 -brine activity can decrease strength and elastic moduli while enhancing porosity and permeability. However, further research is needed to fully understand the impact of CO_2 on rock strength, necessitating comprehensive rock mechanical laboratory testing.

CO2 injection induces various alterations, including cement dissolution, deformations, and changes in transport and elastic properties. These modifications are influenced by site-specific factors such as mineral composition and reactive minerals. Insights from field-scale tests, laboratory studies, natural analogue sites, and numerical models help understand these complex interactions and geomechanical responses. Numerical simulations contribute to the comprehension of coupling phenomena.

The impact of CO2 injection on chemically altered carbonates in storage projects is explored, focusing on reservoir and caprock integrity. Altered samples typically exhibit reduced failure strength and elastic moduli. However, understanding the chemical alteration processes remains challenging, necessitating advanced models that consider formation characteristics.

Studying the dissolution of CO2 in pore fluids and its mechano-chemical interactions with rock minerals reveals changes in porosity, permeability, elastic moduli, and strength characteristics. Laboratory experiments provide valuable insights, but accurate assessments require accounting for site-specific conditions and reservoir-scale heterogeneities. The containment's integrity relies on undamaged caprocks and sealed faults, emphasizing their crucial role.

Cyclic stress loading and unloading on sandstone permeability for underground gas storage is investigated, showing reduced permeability at higher stress levels due to pore space compression. Geomechanical processes, including stress-and-strain changes, microseismic events, and mechanical changes at high pressure, highlight the complexity involved in CO₂ storage projects. Numerical simulators and monitoring techniques aid in analyzing and predicting geomechanical issues.

The importance of considering hydrogeological, geochemical, and geomechanical processes in accurate predictions for CO_2 sequestration models is emphasized. Particle flow models and exploration of different rock formations enhance understanding of fracture propagation and fluidsolid mechanical effects. Computational analyses and dynamic models are necessary to improve accuracy in geoenvironmental systems impacted by CO_2 sequestration.

Interactions between CO₂ and clay minerals play a significant role in caprock effectiveness and well sealing for CO₂ storage. The sorption and swelling behaviors of CO₂ in clays are investigated, highlighting advantages of adsorption over bulk phase storage. Molecular dynamics simulations and experimental studies provide insights into CO₂/clay interactions and their impact on CO₂ trapping, diffusion, and storage safety.

Overall, this literature review emphasizes the need for multidisciplinary approaches, sitespecific considerations, and advanced models to accurately assess and optimize CO_2 storage projects. Further research and comprehensive investigations are necessary to enhance our understanding of CO_2 interactions with reservoir rocks, caprocks, and clay minerals, ensuring the long-term success and safety of CO_2 storage initiatives in the transition to a low-carbon economy.

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1. Introduction

Large volumes of fluids can be stored within rock formations. Several researches studying different aspects of this have been done and are still being done for different purposes. One of the main purposes is to minimize and if possible, eliminate future anthropogenic damage to the environment through storing greenhouse gasses in underground formations. Another reason is the large-scale storage for energy storage integrated via green energy sources. This would also make it possible to take into consideration the novel power-to-gas concept, balancing energy supply and demand, enhancing energy security, and better managing the energy network. Because it makes it possible for substantial quantities of the greenhouse gas, carbon dioxide, to be sealed off in the underground space, it also facilitates the transition to a low-carbon economy. The storage of N_2 , H_2 , and CO_2 can all take place in the same geological formation.

1.1. Underground gas storage

Different rock formations have potential for underground energy storage, leading to competition for the utilization of underground spaces for this purpose. When choosing a geological formation, Matos et al. (2019) suggested taking into account a number of variables, including reservoir geology, energy density, technological efficiency, and sustainable underground space planning, among others. Research was done and a methodology was proposed by Carneiro et al. (2019) to find potential geological formations for massive renewable energy storage in Portugal. Geological structures in porous rocks or caves created in rock salt can be used to store gases like H₂, N₂, and CO₂. Geological traps where oil and gas reservoirs have built up as well as elevated anticlinal structures in aquifers are examples of places where these formations naturally occur. However, some buildings are the result of human action. Three different types of geological formations—deep aquifers, depleted hydrocarbon reservoirs (natural gas and crude oil), and salt caverns—can be used for underground gas storage, including H₂, CH₄, and CO₂.



Figure 1. The three kinds of geological formations used for underground storage. (edited from <u>as-</u> schneider.blog/2021/12/09/natural-gas-storage-in-salt-caverns-and-the-challenge-of-hydrate-formation)

But the behaviour of subterranean gas storage can be more complicated than expected, placing restrictions on the utilisation of particular geological structures. The suitability of a geological formation for underground gas storage is influenced by a number of elements, such as the surface constraints and subsurface geological conditions. When designing and building underground gas storage facilities, it is essential to identify and choose suitable sites. The general geology of the region, rock types, structural and tectonic factors, seismic risks, hydrogeological and geothermal concerns, physical and chemical properties of the stored gas affecting its behaviour in underground spaces, as well as geotechnical factors are among the geological criteria that must be taken into account (Tarkowski et al., 2021).

1.2. Storage in aquifers and hydrocarbon reservoirs

Gas storage in porous rocks underground utilizes empty spaces present in various sedimentary rock types. Rocks with a high degree of porosity and permeability are suitable for storing gas. Porosity refers to the volume of available space within the rock, which can be utilized for gas storage. Permeability, on the other hand, determines the rock's ability to allow gas to flow through it, influencing the injection and collection rates. Deep, highly salinized aquifers that are unfit for drinking or depleted hydrocarbon reserves, which include natural gas and crude oil, can

serve as these storage locations. The underground storage should be surrounded by lowpermeability rocks known as cap rocks, which act as a protective barrier to stop gas from escaping towards the surface (Tarkowski et al., 2021).

Nearby oil or gas fields that have been used up are frequently used as storage facilities. Utilising existing wells, collection systems, and pipeline connections allows a field to switch from production to storage duty. Due to their extensive availability, depleted oil and gas reserves are frequently used as underground storage locations.

Aquifers found naturally have also been transformed into gas storage reservoirs. An aquifer needs to have a water-bearing sedimentary rock formation covered by an impermeable top rock in order to be useful for storing gas. Although aquifers and depleted producing fields have comparable geological features, more base gas must typically be used and withdrawal and injection performance must be more closely monitored.

In comparison to their working gas capacity, salt caverns offer much higher withdrawal and injection rates. Their base gas needs are quite modest. Although building caverns is more expensive than converting depleted fields, the cost of injecting and withdrawing each thousand cubic feet of gas is less expensive per unit since it is possible to do numerous withdrawal and injection cycles per year. (Brun & Allison, 2022)

1.3. Experience in underground gas storage

At present, we have a good experience in underground natural gas storage (UGS), encompassing both porous formations and salt caverns. Over the years, the oil industry has routinely injected liquids into rock formations, reservoir waters, and acid gases like H₂S and CO₂. As of 2018, there were a total of 662 UGS sites worldwide, with a collective capacity of 421 billion Nm³. The majority of these storage sites, accounting for 73.4% (486 sites), were situated in depleted hydrocarbon reservoirs, followed by salt caverns at 15% (99 sites), and aquifers at 11.6% (77 installations). However, when it comes to hydrogen storage, practical experience remains limited. While the knowledge gained from underground natural gas storage can be extrapolated to other gases, the unique properties of hydrogen require further investigation and experimentation before implementing this technology on a large scale. Notably, the first salt caverns dedicated to storing pure hydrogen were constructed in the early 1970s near Teesside, United Kingdom, and

they are still in operation today. Additional hydrogen caverns were built in the United States in the 1980s and in Texas around the turn of the millennium, primarily serving the petrochemical industry. The Russian aviation industry also utilizes several underground storage sites for pure hydrogen. Furthermore, we have more experience in storing hydrogen-coal mixtures (town gas). For example, notable examples include the salt cavern storage site in Kiel, Germany, the aquifer gas-storage reservoir in Lobodice, Czech Republic, and the Beynes storage unit in France.

Injecting CO_2 into reservoir rocks for enhanced oil recovery has been a common practice in the petroleum industry for many years. Currently, the geological storage of carbon dioxide (CCS) in rock formations is being considered as a means to reduce human-caused emissions of this gas. There are several research and industrial installations worldwide dedicated to underground carbon dioxide storage, including Sleipner in the North Sea, Snøhvit in the Barents Sea, In Salah in Algeria, and Weyburn in Canada.

Multiple demonstration projects in Europe and around the world, which are either in the design or operational phase, aim to showcase the feasibility of injecting hydrogen from Power-togas installations into the gas network. This approach offers numerous advantages as it enables the integration of electricity and gas systems, allowing excess electricity generated from renewable sources to be stored as gas. (Tarkowski et al., 2021)

1.4. The reasons of storing the gases in underground reservoirs.

1.4.1. CO₂.

There have been several reports of climate change in recent years, including an increase in the frequency of abnormally warm years, rising water levels, and the melting of snow, ice, and permafrost in regions that supposed to be permanently frozen. Since Arrhenius predicted this phenomenon more than a century ago, it is now generally acknowledged that many of the alterations mentioned are predominantly attributed to the natural greenhouse effect being amplified by rising carbon dioxide (CO₂) and other gas concentrations. (Arrhenius, 1896).

Global Circulation Models, which are intricate computer simulations of the atmosphere that are used in conjunction with models of terrestrial ecosystems and, most significantly, models of the oceans to predict what might happen to the climate. According to these models, if emissions keep increasing, global temperatures may rise by 3–4°C by the year 2100 (Boden and Blasing, 2011). However, there is a lot of uncertainty surrounding this prediction, both in terms of future

emissions and the sensitivity of the climate to rising greenhouse gas concentrations. Further change is anticipated after 2100, and the rate of change may quicken, which raises even more concerns.

The technology would be applicable to big plants, like those that produce electricity using fossil fuels, as well as other industries that reliance on fossil fuels, and would allow for significant reductions in emissions. The use of CO₂ capture and storage (CCS) would make it possible to maintain the current energy supply system, which is crucial given the abundance of existing plants and the vast amount of pertinent knowledge and technical expertise. CCS may also aid in the production of electricity or hydrogen, two viable renewable energy sources derived from fossil fuels with reduced emissions (Gluyas & Mathias, 2013).

1.4.2. $H_2.$

Today's energy source, fueled by combustion of fossil fuels, significantly affects the environment. However, the availability of these fuels is decreasing as global energy demand rises rapidly. The quest for alternative energy sources is driven by factors like energy poverty, climate change, depletion and concentration of fossil fuel resources, and health issues. Recent researches on alternative fuels aim to reduce society's dependence on fossil fuels and foster sustainable economic and social development.

The non-conventional, renewable energy sources like solar and wind power will always be accessible. However, because green energy sources are by definition intermittent, it is necessary to store any excess electrical energy generated so that it can be used when there is a high demand for energy. The creation and subsequent storage of hydrogen is one of the options for storing excess energy (Carriveau & Ting, 2016).

As being a good energy carrier, hydrogen can be generated through a method called peak shaving, which produces hydrogen from surplus green energy. In the field of transportation, hydrogen is viewed as an option to fossil fuels. Peak shaving, however, necessitates large-scale storage solutions, orders of magnitude bigger than those frequently mentioned in connection with mobility, transportation, and other applications. There has never been a pilot test on hydrogen storage sites aside a few case studies and projects (Hassannayebi et al., 2019).

1.4.3. N₂

Injecting and storing CO_2 in water-flooded or depleted oil reservoirs is an effective method for capturing and storing carbon while also enhancing oil extraction. However, the heterogeneous distribution of reservoir properties and the tendency of CO_2 to flow through high-permeability channels limit its burial capacity. To address this, innovative approaches are required. On the other hand, N₂, in comparison to CO_2 , has low solubility in oil, leading to a high interfacial tension with oil. This high interfacial tension makes N₂ more resistant to flow along large pore channels, resulting in more gas flowing along small pores and displacing more oil from small pores compared to CO_2 flooding. N₂ flooding can cover a larger gas swept area due to the high interfacial tension, but it's not as effective in displacing oil from large pores due to the high oil-gas interfacial tension. Laboratory studies have indicated that the application of nitrogen (N₂) flooding on water-flooded cores has demonstrated a modest enhancement in oil recovery, resulting in an increase of less than 10%.

Researchers have proposed N₂ injection alternating CO₂ injection to improve gas sweeping efficiency and enhance oil recovery in complex pore networks of oil reservoirs. Testing was conducted in Japan using CO₂-N₂-CO₂ alteration flooding and showed that the pre N₂ slug can temporarily improve the CO₂ injection capacity by four times. Other studies have investigated N₂ alternating CO₂ injection for EOR and maintaining pressure in heterogeneous oil reservoirs but did not report on gas production and CO₂ storage. Although several studies have investigated N₂ alternating CO₂ injection, the conclusions are not instructive for CO₂ storage (Li et al., 2023).

The entry pressures in cap-rocks limit over-pressures in CO_2 storage operations. Nitrogen injection prior to CO_2 injection in a zone below the cap-rock could increase storage safety by reducing leakage risk and increasing the maximum allowable reservoir pressure. Nitrogen has high N₂-brine interfacial tension, which can increase the allowable pressure by a factor of two, but this also reduces the storage volume and must be studied carefully (Bossie-Codreanu, 2017).

2. Literature review

The objective of storing gas underground is to ensure that it remains there for a specific period of time. Therefore, it is crucial to thoroughly assess and understand the integrity of the storage site before starting the injection process. In particular, it is necessary to carefully examine any potential paths through which gas leakage may occur. There are several mechanisms that could contribute to the escape of gas from subsurface formations. When gas is injected, the rise in fluid pressure may lead to fault activation or fracture in the cap rock formation or storage reservoir. Additionally, the rock may become weak due to chemical processes like the breakdown of carbonate cement or the subcritical expansion of cracks. It is crucial to precisely assess the effects of gas-saturated water on the mechanical features of the host formation, both physically and chemically. (Gluyas & Mathias, 2013)

2.1. Tensile strength and the impact of CO_2 .

A study provided by Ojala (2011) examined the tensile strength of several reservoir and cap rock equivalents utilising Brazilian test procedures. By placing rock discs in salt water that has been saturated with CO_2 , researchers looked at how CO_2 affects tensile strength. Rock samples that had been aged in salt water were evaluated in the same way as CO_2 exposed samples.

Due to the lack of adequate field cores, the author first decided to use Bentheimer and Castlegate sandstones as reservoir rock counterparts. The author also looked at the impact of CO₂-water on carbonate rocks in addition to sandstones. Lixhe chalk and Austin chalk were selected as the representatives for this.

The author adhered to the International Society for Rock Mechanics (ISRM) criteria for specimen diameter and length to diameter ratio to guarantee uniform testing conditions. By measuring the weight and volume of the specimen, the porosity of the rock was identified. All samples were aged in CO₂-saturated seawater (3.5% NaCl) for a week before to testing in an effort to replicate reservoir conditions. The same circumstances were used to age a control group, except they were not exposed to CO₂.

The specimens used in the tests, their average tensile strengths and the results of tests are provided in the Table 1.

Specimens	Average tensile strength (MPa)		Popults
specificits	CO ₂ -water	water	icours
Castlegate sandstone	0.61	0.65	The lower tensile strength in CO ₂ -water samples may be due to lower initial porosity of the sandstone.
Bentheimer sandstone	2.4	2.6	The differences in tensile strength between the two environments could also be influenced by porosity differences.
Austin chalk	1.45	1.8	Tensile strength of Austin chalk varied with porosity and correlated positively with p-wave velocity.
Lixhe chalk	0.66	0.55	Tensile strength did not depend on porosity in the tests. Water- saturated samples failed due to aging, while CO ₂ exposure strengthened porous chalk with low quartz content.
Pierre shale	0.65	0.70	CO ₂ environment had minimal impact on the mechanical properties of Pierre shale, with slight variations in tensile strength likely attributed to natural rock strength variability in shale.

Table 1. Tensile strengths of specimens used in the tests and the results of the tests.

The CO_2 atmosphere did not seem to have an impact on the tensile strength. According to the research, p-wave velocity and rock porosity both influence tensile strength. Such a link was also seen in earlier tensile rock strength experiments. With rising sample porosity, they saw an exponential decline in tensile strength. In experimental tests, the porosity and p-wave velocity have also been found to be correlated with the uniaxial compressive strength (UCS) of sedimentary rocks. These correlations may be used to log or seismic data to derive strength characteristics. In fact, one may anticipate that, as in these studies, both UCS and tensile strength would exhibit a similar reliance on other rock parameters like porosity. This is because the uniaxial compressive strength and tensile strength are predicted to be correlated by the planar Griffith criteria. Important geomechanical metrics, such as UCS and tensile strength, are utilised to calibrate numerical models of the reservoir and cap rock system during CO₂ storage. The fracture pressure and subsequent likelihood of leaking during injection or long-term storage are predicted by the tensile strength. These models need as their input data strength parameters that have been empirically measured on CO₂ saturated rocks. The conserved core material from a storage location must thus undergo rock mechanical laboratory testing. Therefore, it is predicted that a more complete investigation of the impact of CO₂ on rock strength will take place (Ojala, 2011).

2.2. CO₂-brine-rock interaction in the process of geological storage.

One of the promising ways of achieving net-zero goal is CO_2 storage in geological storages. But to fully comprehend and control of CO_2 storage, it is vital to investigate the effects of CO_2 on the geological formations, if it improves or deteriorates the storage capacity. One of the researches studied this has been performed by Peter et al. (2022) which I am going to review in this section. The subject matter of this review includes the impact of all CO_2 -brine phases on the petrophysical, mineralogical, geomechanical, and physical properties of reservoir rocks, as well as the ramifications for reservoir behavior and storage procedure effectiveness.

The study states that, the effectiveness of CO_2 storage depends on the properties of rocks, but when CO_2 , brine, and rocks interact, it can negatively impact storage ability. It's important to understand the pressure-temperature conditions, solubility, phase behaviour, and thermodynamics to address this. CO_2 and brine can coexist in the reservoir with undissolved CO_2 phases that can affect rock properties. The type of CO_2 phase present in the reservoir influences the interaction between CO_2 , brine, and rocks.

The authors focused on mainly saline reservoir, however, the capacity of other reservoir types and their comparison with reservoir type of interest is briefly discussed. Based on several studies the saline reservoirs offer good storage potential in means of capacity, meanwhile not all saline reservoirs are suitable like onshore ones due to usages for agriculture and groundwater exploitation. Also, saline reservoirs have some cons like the necessity of building infrastructure, meanwhile depleted oil and gas fields have already; pressurization due to injection. While selecting an appropriate reservoir, there are other factors that should be taken into account.

The study also includes list of studies which learning the effects of pressure, temperature, composition of the brine, impurities from flue gases, etc. by applying numerous methods and models was discussed. Most of them pointing out that the solubility of the CO₂ is affected negatively by temperature, salinity, and pH, meanwhile pressure increase positively affects the solubility.

Because there is a relationship between the reservoir's chemical and mechanical characteristics, any change in the chemical composition will have an impact on the rocks' bulk modulus, strength, and elastic modulus. Several sources has been provided that validates this. Consistent monitor of the sequestration site is sensible as CO₂-brine can lead to weaking of rocks and dissolution of minerals.

CO₂ affects caprocks differently as they differ in composition and mechanical properties compared to the rest of the reservoir. During CO₂-brine-rock processes precipitation and dissolution are one of the observed processes which have weaking effect on rocks, which means it downgrades geochemical and geomechanical properties of the rocks. Based on several observations carbonates are considered better reservoirs for CO₂ storage.

Based on researches CO_2 -brine activity, in general has negative impact on strength, elastic modulus, and bulk modulus, meanwhile porosity and permeability are improved. But the duration of residency of CO_2 -brine plays important role in the undergoing processes and so, depending on the time different outcomes should be expected. Concluding all the results from different researches, even if the little time period given to observe the impact of CO_2 on reservoir rocks in comparison to real time needed to fully understand them, the changes appear in very beginning of the experiments (in hours or sometimes days) and progress as time passes. They explained this with continuous increase of acidity of brine. Also, it is stated that this experiments cannot fully demonstrate how real geological storage will interact with CO_2 , since this interaction is site-specific and a variety of elements are relevant.

The study with application of microscopic rock image analysis found that the properties of reservoirs are affected differently by supercritical CO₂-brine and gas-phase CO₂-brine states. Supercritical CO₂ alters the topology of minerals by causing fines to precipitate and grains to aggregate, as well as the shape and flatness of pore surfaces. It also causes a rise in secondary fatigue rate and a fall in bulk modulus and shear strength. In the meanwhile, stress-induced decreases in permeability and porosity as well as changes in the topology of minerals are being caused by gas-phase CO₂. But for all samples, compression resulted in increase in smoothness of grains and pores, whereas the roundness increased for grains and decreased for pores.

At the end, the authors point out that different researches used a range of approaches applying different imaging techniques are conducted aiming at studying the rock properties evolution during the storage. Also, most of the experiments are conducted for short-term and as they provide limited knowledge, it is necessary to study long-term experiments to have full comprehension of undergoing processes. Precipitation and migration phenomena are considered having great importance by authors, as they cause integrity changes in geological storages (Peter et al., 2022).

2.3. Coupled chemical-mechanical processes related to the injection of CO₂ into the subsurface.

Predicting the long-term subsurface processes that take place during CO_2 storage is crucial to the effectiveness of geological carbon storage. Understanding the mechanical changes in deep geological carbon storage units brought on by CO_2 injection, particularly in connection to the chemical modification of the medium, is essential to making this prediction. These chemicalmechanical coupling events can take place over a variety of length and timelines, but it is yet unclear how and where they affect the system's capacity for storage and overall safety. Examining the effects of geochemical and geomechanical disturbances brought on by CO_2 injection on the effectiveness of geological carbon storage is crucial in this context.

The paper published by Ilgen et al. (2019) is reviewed and found well explanatory for this topic. A sizable amount of research is reviewed by the publishers in order to comprehend the associated geochemical and geomechanical processes of CO₂ injection into geological formations. They grouped them under 4 headings, which are field scale tests, laboratory studies, natural analogue sites, numerical models. Each of them provides insight of the undergoing processes inside the rock formations in their own unique way. But each of them has one common focus to understand how chemical and mechanical processes will weaken the reservoir formation and how will affect the reservoir capacity.

In field scale tests several already existing CO_2 injection test and their results have been reviewed. Based on findings in one site, minor calcite dissolution process appears. It is suggested that the model based on classical rock-physics cannot predict the recorded changes in P-wave velocity (a proxy for the shear moduli) observed in the time-lapse seismic data collected during the test, which can be explained by changes in rock microstructure, specifically the removal of cement at grain contacts.

In another site test the permeability is increased just after the CO_2 injection started which is believed as a result of fracturing which is a geochemical process. Also, chlorite cement is found susceptible to dissolution due to its nanoscale porous connected channels and it is related to previous observations (fracturing).

The laboratory experiments are also reviewed and they are good for short length-scale, timescale-focused testing of coupled chemical and mechanical processes. But due to obvious

reasons, this kind of experiments cannot be conducted for slow rock formation response observations.

The reviewed laboratory tests are done on variable rocks each simulating different reservoir conditions, brine and supercritical CO_2 injection conditions, high or low pressure and temperature conditions. Each of them focused on various rock and cement alterations, but most commonly cement dissolution and rock deformations are studied.

The test studying changes in the transport and elastic properties of rocks due to CO_2 injection observed changes in the microstructure, including enlarged pores and increased porosity. Chalks were found to have the most alteration, with changes in S- and P-wave velocities indicating changes in bulk and shear moduli. Calcite dissolution resulted in mechanical compaction under pressure.

Tests done to understand mineral dissolutions demonstrated interesting results. Scratch testing done on altered rocks found out that sandstone can lose its hardness, scratch toughness and strength up to 2 times, but under same conditions siltstone degrades more. Other studies demonstrated that quartz cementation is less susceptible to dissolution than calcite cement due to its grain-to-grain contacts, meanwhile chlorite-cemented lithofacies are the least desired thanks to their susceptibility to mechanical degradation. Another study done by Lamy-Chappuis et al. (2016) also supports these findings and additionally stating that there is a positive correlation between porosity and rock mechanical properties.

According to the results of both low- and high-pressure testing, the primary factor causing deformation is pressure solution creep., with chemical reactions at the grain contacts (and consequently chemical dissolution rates) controlling the deformation of the system.

Mixed illite/smectite illitization can happen under circumstances that are relevant to the geological storage of carbon. It has been demonstrated through experiments with K-feldspar in batch and mixed-flow reactors that proton-promoted illitization is more pronounced in acidic solutions. This process may take place in mixed illite/smectite-rich caprock lithologies. Adsorption to high surface-area clay minerals may provide an additional sink for CO₂, and CO₂ intercalation into clay mineral interlayers can occur. CO₂ exposure can lead to extensive cracking of biotite mica and dehydration cracking of smectite clay minerals in the caprock. However, research on the mechanical consequences of geochemical alteration of clay minerals due to CO₂ exposure is limited due to slow reaction kinetics, making it difficult to assess at laboratory timescales.

In the paper natural analog sites, which are locations where carbon dioxide (CO₂) has been naturally emplaced and retained in the subsurface over long periods, are mentioned and stated that They can offer useful information about the long-term impacts of CO₂ on rock assemblages and geomechanical properties. Based on several examples of such sites in many parts of the world, it is observed that some sites exhibit frequent CO₂ leakage, while others retain CO₂ in the subsurface over geologic timescales.

Based on research at natural analogue sites, it appears that the specific geologic setting affects how long-term CO₂-brine-rock interactions affect the mechanical characteristics of rocks in different ways. The studies described show a range of outcomes, from no significant mechanical weakening observed in CO₂-altered Navajo Sandstone at the Green River natural analog site (Busch et al., 2014) to significant mechanical degradation observed in CO₂-altered Entrada Sandstone and Summerville Siltstone at the Crystal Geyser site (Aman et al., 2017; Sun et al., 2016a).

The studies also suggest that factors such as the mineral composition of the rock, the distribution of reactive minerals, and the presence of protective coatings can all play A role for figuring out how much and nature of mechanical degradation caused by CO₂-brine-rock interactions. For example, Hangx et al. (2015) found that porous and permeable sandstones with low amounts of reactive minerals were particularly vulnerable to mechanical effects, while cement distribution and strength controlled the overall degradation of mechanical properties in sandstone altered by CO₂ and brine.

Overall, the results indicate that to effectively forecast the effects on rock mechanical characteristics, a more in-depth comprehension of the unique geologic environment and the mechanisms involved in CO_2 -brine-rock interactions is required. The use of different methods to quantify mechanical degradation, as seen in the contrasting conclusions of Busch et al. (2014) and Sun et al. (2016), further highlights the need for a comprehensive and multidisciplinary approach to studying this phenomenon.

The researches reviewed above highlights the importance of considering length scale when analyzing chemical-mechanical effects. As natural rock sites have uneven permeability, geochemical changes are concentrated in high-permeability zones. Similarly, heterogeneity affects geomechanical reactions to CO_2 injection, with variable results at different length scales.

Another section of the paper discusses various numerical simulations conducted to study the coupling of geochemical and geomechanical processes during carbon dioxide capture and storage (CCS). The authors first highlight the challenges faced in laboratory experiments and field-scale tests due to the vast spatial and temporal scales of the processes involved. Then they provide examples of studies that use numerical simulations to understand the impact of various parameters on the CCS process.

Tian et al. (2014) used numerical simulations to study the impact of heterogeneity in permeability and porosity on caprock integrity. Morris et al. (2011) combined reservoir modeling and InSAR observations to model surface deformation observed during CO₂ injection. Newell et al. (2016a) used field data to investigate the impact of thickness and wellbore orientation on caprock integrity. Cappa and Rutqvist (2011) investigated fault reactivation using hydromechanical models. Martinez et al. (2013) constructed a coupled multi-physics model to study the effect of injection pressure on caprock integrity.

The authors also highlight the limitations of numerical simulations, including computational cost, complexities in model verification and validation, and difficulties in addressing the multiscale, multiphysics aspects of the simulations. They conclude that it is not practical to integrate all geomechanical and geochemical effects into a single model while preserving numerical efficiency and accuracy. Therefore, researchers are using various numerical approaches to understand the coupling phenomena.

In the final section, it is discussed how crucial it is to comprehend coupling phenomena, such as chemical-mechanical coupling, while performing numerical simulations of geological carbon storage. Different models proposed to simulate these phenomena in carbonate rocks, including the identification of geochemical variables such as mass and volumetric swelling of minerals that are affected by chemical reactions, and describes how to model chemoplastic deformation processes.

The authors present examples of different approaches to modeling the coupling between chemical reactions and mechanical properties, such as chemoelectroplasticity, chemoplasticity, and chemoelasticity. They also highlight the need to upscale the resulting relationships to arrive at a continuum scale that can be implemented into computational codes.

They highlight that the consistency of the multiphysics, multiphase, and multiscale modeling approaches plays a critical role in the numerical assessments of GCS. One possible method of modeling coupled chemical-mechanical-hydraulic processes in carbonate rock is by proposing specific mechanisms, in which models of individual classical features such as elasticity, plasticity, or permeability depend on appropriate geochemical variables. These variables may include the mass of the entire rock or a dominant mineral fraction dissolved/precipitated within a representative volume from/at a specific location. The evolution of these variables can be described using various laws and models, such as geomechanical contact cement models, chemical reaction rate laws, osmotic diffusion equations, and adsorption laws. These laws are formulated on a micro-scale model, with the variables and characteristic dimensions related to the scale of intergranular bonds.

Chemoplastic deformation processes, driven by ion concentration changes or mineral mass dissolution/precipitation, have been modeled by various researchers. For instance, Homoionic chemoplasticity is applied to clay swelling by Loret et al. (2002), while chemoelectroplasticity addresses ion exchange-driven swelling in heteroionic clay minerals in Gajo et al. (2002). Nova et al. (2003) modeled chalk dissolution and resulting brittle-to-ductile transition. Hu and Hueckel (2007) examined a pressure solution model for silicate rock dissolution, with subsequent short-distance transport and precipitation in a closed system using a scenario of intergranular indentation and compaction. They employed a rigid-plasticity model with strain hardening and chemical softening due to mineral mass removal enhanced by irreversible damage at the micro-scale.

An alternative approach to chemical-mechanical coupling in rocks is through differentiation between the dissolution/precipitation of intergranular bonds and grains. An example includes the case for calcite cement within sandstone. A formulation with an explicit characterization of geometrical parameters of interparticle bridges has been proposed by Gajo et al. (2015).

The authors also highlight that chemoplastic coupling in rocks is a significant factor in determining failure and damage conditions. For example, Hu and Hueckel (2013) modeled the propagation of subcritical fracture induced by carbonate dissolution in prestressed, calcite-rich material in the process zone around the crack tip. They coupled the dissolution of calcite with irreversible straining (microcracking), while the latter is coupled to the dissolution rate, predicting the rate of fracture propagation while linking it to the calcite dissolution rate (Ilgen et al., 2019).

2.4. Petrophysical and geomechanical properties of carbonates affected by chemical alteration.

A CO₂ geological storage project's ability to succeed hinges on maintaining the injectivity and integrity of the site. Contrary to normal gas injection, CO₂ injection causes geochemical processes that change the reservoir and cap rock's petrophysical and geomechanical characteristics. The research conducted by Bemer and Lombard (2010) highlights the experimental difficulties in studying the low-permeability specimens of the cap rock or zones of transition from the reservoir to the actual cap rock. The effects of acidification brought on by CO₂ injection on carbonate samples are investigated by the authors using a chemical modification process. When injectivity and integrity concerns are taken into account, the experimental data show tendencies of chemically induced mechanical weakening.

The first section provides detailed information about three types of limestone (Comblanchian, Lavoux, and transition zone) that are being considered for CO₂ injection. The Comblanchian limestone comes from Charmottes field, and the Lavoux limestone comes from a Dogger outcrop, while the transition zone samples are also from Charmottes field. The section includes information on the porosity and steady-state brine permeability of each type of limestone, as well as the composition of each rock. The authors also note that porosity measurements for compact argillaceous rocks, such as the transition zone limestone, can be difficult to obtain using weight measurements due to bound water interfering with achieving a dry state. NMR measurements can be used instead, but there may be differences in the porosity values obtained through these two methods.

By use of homogeneous alteration method, authors did experiments to alter rock samples. The method is based on the injection of a retarded acid solution that is activated only under specific temperature conditions. The experimental setup, including the core holder and the associated processes, has been extensively described in a previous publication.

The alteration process involves several stages, including flushing the sample with fresh retarded acid at ambient temperature, activating the acid under specific temperature conditions, and then flushing the sample with fresh brine at ambient temperature. The number of successive acid treatments controls the final alteration level. The petrophysical properties of the samples are characterized before and after alteration, including porosity and steady-state permeability measurements.

The paper notes that for standard reservoir rocks, a whole alteration step can be carried out in one day. However, for low permeability samples, the time required to substitute brine for acid and acid for brine becomes a major issue. Higher injection pressures have been used to avoid too long-lasting tests, but this can lead to more marked end effects, and the damaged part of the sample may need to be cut away prior to doing the triaxial test. The paper also notes that for the lowest permeability sample tested, it took more than one month to achieve six successive acid treatments, highlighting the potential for dramatically increased test duration for effective cap rocks with lesser permeability levels.

The research offers insightful information regarding how chemical alteration affects the porosity and permeability of limestone samples. The authors conducted experiments on Lavoux samples, altered through standard and retarded acid treatments, and observed improvements in surface evenness provided by the retarded acid method. CT-scanner observation corroborated the homogeneity of the pore structure evolution. The porosity values calculated from CT-scanner observations were consistent with the other measurements, indicating that the CT-scanner porosity is a reliable measure of porosity.

The data that authors have presented illustrates the chemically induced increase in porosity for the altered samples. The results suggest that one retarded acid treatment leads to an additional porosity of approximately 0.3%-0.4%, and three and six RAT can result in about 1% and 2% additional porosity, respectively. The intrinsic dispersion of samples' initial porosity and altered porosity values have been compared with the overall intact porosity range of each studied formation, and caution has been advised when considering results obtained on altered samples, which show a porosity remaining in the overall intact porosity range of the corresponding formation.

The authors have also provided information on the permeability variations associated with observed porosity increases. The results suggest that the permeability variations do not follow a clear trend, and further experiments are needed.

To realize the geomechanical characterization of the intact and altered carbonate formations, the authors conducted triaxial tests and provided the methodology and results of the tests. The authors employed standard procedures to assess the geomechanical properties of the samples, focusing on effective stress, pore pressure, and failure criteria. The authors utilized cylindrical plugs of the carbonate formations and equipped them with strain gauges for axial and radial strain measurements. The samples were coated with an impermeable jacket to ensure independent control of confining and pore pressures. The stress state was maintained as axisymmetric, defined by pore pressure, confining pressure, and axial stress. The test results were analyzed in terms of effective mean stress and deviatoric stress, as rock failure is governed by Terzaghi's effective stress.

To ensure proper saturation, the samples were first saturated with an inert mineral oil. The saturating fluid was injected under pressure, and equilibrium of pore pressure was achieved at both ends of the sample. To overcome the challenge of low permeability in transition zone samples, a reversal of the injection direction was sometimes necessary to ensure the breakthrough of the pressure front. The mechanical loading induced excess pore pressure generation, and the tests were conducted under mixed drainage conditions to record pressure variations within the sample.

The authors identified drained elastic moduli and failure points in the p'-q diagram as key parameters to assess the effects of chemical alteration. The confining pressure level corresponding to the transition between brittle and ductile failure was determined to understand the behavior of intact and altered samples. The failure behavior of different formations was consistent, with samples of lesser porosity generally exhibiting greater strength. Brittle failure was observed for effective confining pressures less than or equal to 12.7 MPa, while ductile failure occurred above 20 MPa.

Additional tests were performed on intact Lavoux samples to evaluate intrinsic scattering of rock failure properties and determine bounds for the confining pressure level. Based on authors' findings, In the p'-q plane, it can be observed that failure points exhibit consistent behavior across various formations. Additionally, when measuring intact elastic moduli during axial unloading stages, wider scattering and lower stiffness are seen in transition zone samples compared to Comblanchian and Lavoux samples. This difference in behavior could potentially be attributed to the presence of argillaceous fraction.

A detailed analysis of the effects of chemical alteration on the geomechanical properties of carbonate rocks has been provided too. The authors examined the impact of chemical alteration on the shear strength and elastic moduli of the rocks.

By presenting experimental data in the form of stress paths and failure points for intact and altered samples, they note that pore pressure variations during triaxial tests on transition zone

samples lead to non-linear stress paths, and that there is significant data scattering associated with these samples. However, for most of the samples, the authors find that chemical alteration leads to a clear decrease in the failure strength of the rocks. The elastic moduli of the samples are examined and it is found out that altered samples, including those from the transition zone, generally have lower average elastic moduli than intact samples.

The authors then compare the experimental data to theoretical models based on empirical variation laws linking carbonate elastic and failure properties to porosity level. The models allow the authors to estimate the expected variation in strength and stiffness between two natural samples of the same rock type and with similar porosity differences. The authors find that the range of variation allowed by the empirical failure model is too large for the altered samples' strength to fall beyond, suggesting that more advanced models that take into account other characteristics of the studied formations are needed to better represent the effects of chemical alteration.

The impact of chemical alteration on the natural trends of elastic moduli is examined as a function of porosity, by comparing the experimental data to literature data for various carbonates. The decrease in stiffness induced by chemical alteration makes the altered Lavoux samples fall in the model lower half, but they remain within the allowed range. In contrast, the altered Comblanchian samples fall distinctly out of the allowed range, indicating that the irreversible porosity increase induced by chemical alteration lowers their stiffness farther than the natural trend. The authors suggest that differences in the structure and mineralogy of the two carbonates may explain the higher sensitivity of Comblanchian limestone to chemical effects (Bemer & Lombard, 2010).

2.5. The mechano-chemical interactions of weak acid formed by CO_2 storage.

When CO₂ is injected into geological storage facilities, it may dissolve in the resident reservoir pore fluid and form a weak acid, which lowers the pH of the brine and can react with the rock's minerals. Studies have concentrated on CO₂-induced microstructure modifications and their impact on hydraulic and multiphase flow properties. CO₂-induced alteration of rock properties is a significant challenge for assessing storage performance. However, it is also anticipated that mineral dissolution brought on by CO₂ will have an impact on the mechanical characteristics of sedimentary rocks. Rohmer et al. (2016) examine the effects of these dissolution-induced changes on elastic

properties, failure parameters, and time-dependent mechanical behaviour, as well as their potential to result in reservoir degradation, surface subsidence, caprock failure, and induced seismicity.

An overview of the laboratory studies that have been done to look into how CO_2 injection affects rock properties was given by the authors. The authors provide an overview of nearly 40 representative laboratory studies, emphasising the crucial experimental parameters and key findings.

The experiments, which were divided into two types to study dissolution under acidic conditions and static/low fluid flow rate effects on rock's petrophysical and mechanical properties, examined the effects of CO_2 injection on these properties. The range of thermodynamic conditions explored varied from shallow to reservoir conditions up to 5 km depth. The duration of the experiments also varied, with some focusing on fast processes near the injection well and others on the long-term effects of CO_2 on the change in deformation and permeability of the samples. Various rock types were used, including those with enhanced fluid-rock reactions such as carbonates. The experiments also varied in the type of samples used, including rock core samples, aggregates, and artificially pre-cracked core samples. The authors note that the measured effect of CO_2 is often greater for the latter two types of samples because of flow focusing and/or higher reactive surface area.

The authors first focused on the mechano-chemical effects of CO₂ on reservoir rocks. Reviewed numerical simulations show that CO₂ injection in reservoirs can lead to different zones of mineral reactions based on the spatial distribution of gas saturation. These zones include the fully saturated zone near the wellbore (Zone I), a transition zone with a two-phase mixture (Zone II), a zone fully saturated with an acidified aqueous CO₂ solution (Zone III), and a zone furthest from the wellbore considered unaffected (Zone IV). The CO₂-induced dissolution/precipitation phenomena primarily occur in Zones II and III, leading to localized dissolution patterns and potentially wormhole growth, particularly in carbonate-rich rocks (Figure 2).



Figure 2. Scheme of the storage with several zones surrounding the injection well based on CO2 saturation (Rohmer et al., 2016).

Various studies conducted on mechano-chemical effects of CO_2 on reservoir rocks were provided. They cover experiments involving limestone samples exposed to supercritical CO_2 and a saline aqueous solution, as well as the alteration of rock samples using a retarded acid solution. The authors look into how CO_2 's chemical affects on rocks' porosity, permeability, elastic moduli, and strength characteristics.

The first set of studies, conducted by Sterpenich et al. (2009), Grgic (2011), and Rimmelé et al. (2010), explores the dissolution of calcite and its effect on porosity and elastic moduli. The researchers find that the dissolution is limited (<1%), resulting in a non-significant variation in porosity and no changes in the velocity of ultrasonic waves. The opposing effects of CO₂ and pH are identified as the reasons for the minor impact, with the increase in CO₂ partial pressure making the solution more acidic but also enhancing the thermochemical stability of calcite.

The authors refer to studies by Egermann et al. (2005), Bemer and Lombard (2010), Nguyen et al. (2011), and Zinsmeister et al. (2013) to understand the worst-case scenario of acid attack on carbonate samples. They investigate the alteration of wackestone and packstone carbonate rocks from the Paris basin, showing changes in porosity, permeability, strength, and elastic moduli. The authors suggest that microstructural differences between carbonate types necessitate advanced models for accurate representation. Nguyen et al. (2011) further develop a micromechanical model to understand the weakening process in carbonate rocks. Zinsmeister et al. (2013) enhance the characterization of limestone by utilizing digital image correlation techniques and X-ray micro-

computed tomography. They find that strain localization depends on the nature of the grains and that failure behavior can shift from brittle to ductile with increasing alteration.

In this part they also touch on experiments conducted on carbonate-cemented and silicatecemented sandstones. The studies suggest slight increases in porosity and hydraulic conductivity for carbonate cement, while the effects on silicate cement are attributed to CO₂ interactions with clay minerals. Secondary carbonate minerals or salts precipitation may mitigate these effects. The geomechanical response of degraded sandstones is variable, with some experiments showing modified elastic deformation behavior and reduced strength parameters.

The authors compare the results of batch-reactor tests with those of flow-through experiments in the following section, emphasising the larger reaction seen in the latter. The samples are exposed to CO₂-saturated reactive brine or a two-phase fluid mixture during the flow-through tests while reservoir pressure and temperature conditions are kept constant. The trials mimic the mass transfers that take place from the injection well in various zones. The authors note that compared to batch reactor tests, flow-through trials cause higher porosity variations.

The section also highlights how rock-fluid interactions are influenced by the original microstructure of the rocks. Heterogeneous dissolution processes are observed at the core sample scale, leading to reactive flow focusing and the formation of wormholes in some cases. By occupying the existing wormhole seeds, supercritical CO_2 prevents the formation of wormholes. The relationship between porosity and permeability is discussed, with different exponents observed for carbonate rocks with homogeneous and heterogeneous microstructures.

The mechanical response of the rocks to chemical alterations is addressed, focusing on changes in elastic moduli and wave velocities. The experiments demonstrate considerable changes in elastic moduli and wave velocities, with the magnitude and extent depending on injection conditions, confining pressure, and rock microstructure. The study highlights the importance of conducting wave velocity measurements under loading to understand the competing processes of dissolution, mechanical removal of particles, and mechanical compaction.

Chalk formations, known for their high porosity, are identified as potential candidates for CO₂ storage. Triaxial experiments conducted on brine-saturated chalk samples show minor mechanical effects, primarily a decrease in stiffness. The effects of CO₂ exposure on oolitic limestone are described as a worst-case scenario, with significant porosity increase, altered elastic properties, and increased susceptibility to collapse.

Tests on sandstones with calcite cement indicate calcite dissolution, leading to increased porosity and permeability. However, the mechanical properties of these sandstones are minimally affected. The authors also mention experiments on anhydrite- and quartz-cemented sandstones, highlighting anhydrite dissolution, calcite precipitation, and salt precipitation as potential outcomes.

The authors highlight that compaction can result from poroelastic compression or timedependent processes known as "compaction creep." They explain that such deformation processes in long term can lead to damage of various parts of the storage system. The process of timedependent compaction, which occurs under high pressure and temperature conditions, involves both mechanical and chemical processes. These processes include elastic strain, cataclastic flow, grain failure and debonding, and stress-induced dissolution-precipitation processes. These mechanisms lead to modification of the mechanical properties of the porous medium and can cause grain crushing, subcritical cracking, and intergranular pressure solution creep.

The studies on the influence of CO_2 partial pressure on carbonate rocks and the role of increased dissolution rates in higher strain rates are mentioned. These experiments involve various conditions and are similar to those in subsurface reservoirs targeted for CO_2 storage. Results show that CO_2 -saturated solutions can cause enhanced strain, with acceleration ranging from insignificant to a maximum increase of ~50 times. The most significant acceleration was observed in wet calcite aggregates with a grain size below 106 µm under specific conditions.

The authors talk about how several factors, including pressure solution creep and subcritical crack formation, affect compaction rates. They point out that the development of subcritical cracks and chemical variables, particularly the activity of water, are important in the spread of cracks. The effect of CO_2 on crack growth is expected to be more prominent near the injection well due to altered water activity and the stabilizing effect of CO_2 .

However, the authors caution against directly extrapolating experimental results to reservoir conditions. They highlight the importance of site-specific conditions, including grain size, pH of the aqueous solutions, temperature, effective stress state, and CO₂ pressure. Factors such as the chemical composition of the pore fluid and the presence of impurities in carbonate rocks can significantly affect pressure solution creep. Additionally, the boundary conditions and sample size in laboratory experiments may not fully represent the heterogeneities and dissolution regimes at reservoir scales.

The paper also mentions studies conducted on sandstones, which indicate a smaller increase in creep rate compared to limestones when exposed to CO_2 -rich fluids. Some studies suggest that the presence of CO_2 inhibits microcracking and decreases creep rate in sandstones.

The authors discuss the limitations of short-term laboratory experiments and highlight the importance of studying natural analogs, rocks that have been in contact with natural CO_2 sources for extended periods. They refer to studies analyzing natural CO_2 reservoirs and other sandstone formations, which suggest that little change in mechanical strength may occur in pure sandstones even after long-term CO_2 exposure.

Evaporite and shale caprocks, two major kinds of caprocks, are examined in this research. The porosity of these caprocks might vary, but their permeabilities are minimal. Evaporite caprocks tend to be less porous than clay-rich caprocks. Clay-rich caprocks' limited permeability is frequently brought on by strong capillary entry pressures. The elements in these rocks that interact with CO₂ include carbonates, organic matter, and swelling clays. Most clay caprocks contain a small percentage of organic matter, and when in contact with dry supercritical CO₂, they experience minor changes in porosity and permeability. CO₂-sorption in clays and clay swelling can potentially increase the sealing capacity of a swelling clay-rich caprock, but if swelling stresses exceed rock strength, it may decrease the sealing capacity.

When the caprock is in good condition, CO_2 can enter it by diffusing through it, reacting chemically with it, or by pushing through the capillary entry pressure of the pores. The permeability of the caprock is influenced by factors such as pore size, wettability, and interfacial tension. Different gases, such as N₂, CO₂, and CH₄, exhibit varying capillary entry pressures.

Experiments indicate that even after the breakthrough pressure is exceeded, preferential pathways for CO₂ exist in the rock, leading to increased gas permeability. However, the permeability of intact clay caprock is found to be similar for dry CO₂, argon, and distilled water. The introduction of CO₂-saturated water significantly increases permeability, suggesting that pore fluid acidification plays a crucial role in caprock integrity.

Geochemical models are used to examine the reactions between CO_2 -saturated brine and caprock. Results from various studies indicate that the porosity changes and reactions are limited to the first few meters of the caprock. The reaction front between CO_2 and caprock is generally of a limited extent, especially for undamaged caprocks, and should not compromise site integrity over long timescales if sufficiently thick caprock is present.

Additional experiments involving cement presence in reservoir rock and clay caprock demonstrate that even with alkaline sources, the extent of the reaction front remains limited. Overall, the findings suggest that undamaged caprocks will only experience a limited extent of interaction with CO₂, typically within the first 10 meters from the caprock-reservoir interface over a timescale of up to 10,000 years. Therefore, selecting sites with thick caprock should prevent breach of site integrity due to the slow progress of the reaction front.

Caprocks, which may appear intact on a seismic scale, can actually have damage on smaller scales. While CO₂ infiltration into intact caprock is challenging, fault zones with damaged rocks could experience stronger effects. Fault zones are common in subsurface reservoirs, including hydrocarbon reservoirs and aquifers, and they can serve as pathways for gas leakage. However, it is noted that not all faults are leaky.

Fault zones consist of a damage zone and a fault core, and the permeability of these zones depends on factors such as grain size, fracture aperture, roughness, and fault zone constituents. Fine-grained gouges have lower permeability compared to coarse-grained gouges. The relative percentage of the fault core and damage zone determines whether the fault zone acts as a barrier or a flow conduit. Additionally, the presence of clay-rich units can decrease permeability even if they are not directly juxtaposed, a phenomenon known as "clay smearing." The porosity and permeability of the fault rock compared to the host rock also play a role in determining whether the fault acts as a barrier or conduit.

Fault slip can cause temporary dilation of a fault zone, leading to a temporary increase in permeability and the potential for gas escape.

A review of natural CO_2 reservoirs indicates that containment is more likely in reservoirs at depths where CO_2 is in its supercritical state and where the reservoir pressure is less than 50% of the lithostatic pressure. Experimental studies on fractured caprock show that fracture permeability is lower for dry CO_2 in its supercritical phase compared to the gaseous phase. The state of CO_2 , combined with the overburden stress, is important in determining whether a fault is sealing or not.

Assuming storage in a sealed site, the response of the system to a reactivation event is another important consideration. The term "sealing" refers to the loss of permeability. Compaction experiments on granular materials, such as quartz, feldspar, calcite, and anhydrite, simulate porosity loss in fault gouges associated with sealing. Some studies indicate that the presence of CO₂ can accelerate creep rate, while others show no significant effect. Estimates suggest that fault

sealing times in anhydrite fault gouges are on the scale of decades or less, much shorter than the total CO₂ storage times.

It is challenging to estimate sealing times for aggregates compacting through subcritical crack growth, and the influence of mixing gouge minerals and the presence of clays and salts on sealing times is not well understood.

In storage projects, there is a considerable likelihood that a fault could reactivate, and determining the risk of this happening is crucial. The likelihood of a defect reactivating due to a change in effective stress or due to the combined action of thermal stresses has been the subject of studies. Large-scale CO₂ storage sites may still be hindered by fault reactivation caused by higher pore fluid pressure, but this issue is still up for debate. Using induced seismicity as a criterion for when faults are reactivated, it has been shown that injection pressure and rates are the main parameters that control fault reactivation, and proper knowledge of the stress and pressure conditions at depth is needed before injection. The possibility of fault reactivation through changing stresses should be evaluated on a case-by-case basis using coupled flow and large-scale mechanical simulations. Depleted hydrocarbon reservoirs are more attractive options for CO₂ storage than aquifers due to their well-known stress state and lower stress state before injection.

The paper also discusses the effect of CO_2 on the frictional strength of fault zones. The experiments showed that CO_2 -saturated water had no effect on gouges made by crushing and sieving two different clay caprocks and one sandstone reservoir rock from the North Sea area. A reduction in friction coefficient up to 15% was found for simulated anhydrite gouges in the presence of water and CO_2 . However, such a decrease in frictional strength does not necessarily lead to fault reactivation. The impact of CO_2 on the friction coefficient in simulated fault gouges derived from sandstone, shale or anhydrite is limited to within a few per cent.

The authors mention that the fault reactivation in storage sites can potentially lead to induced seismicity. The rate-and-state friction law is introduced, which describes how a material generates earthquakes by meeting two conditions: the total stiffness of a system must be less than a critical stiffness, and the material must exhibit velocity-weakening behavior. The velocity-dependence of friction is strongly influenced by various factors such as temperature, normal stress, the presence of pore fluid, and displacement. Three main lithologies, namely quartz-dominated rocks, carbonate- and anhydrite-dominated rocks, and clay-dominated rocks, are discussed, and it is shown that only calcite-dominated faults require attention from the perspective of induced

seismicity, assuming that the velocity dependence of friction is the primary factor in earthquake nucleation.

The effects of CO_2 on velocity dependence in different rock types have been investigated, and it is revealed that CO_2 does not immediately affect the nucleation of induced seismicity in quartz-rich reservoir rock, two clay-rich caprocks, dolomite, or anhydrite. However, the effect of CO_2 -saturated fluid on the frictional properties of calcite-rich fault gouges remains unknown. Testing of simulated quartz-dominated gouges and their unreacted counterparts, derived from a reservoir in which the gas is naturally high in CO_2 content, has shown no increase in seismogenic potential, even after long exposure times.

The paper also discusses the expected long-term chemical interactions between fault rock and CO_2 . The experiments conducted on pre-fractured samples of different compositions under different flow rates and confining pressures reveal that the dissolution of minerals and consequent changes in permeability depend on the composition, microstructures, and flow rates of the samples. For example, the flow-through of CO_2 -acidified brines in an anhydrite/dolomite core leads to the preferential dissolution of anhydrite over dolomite, resulting in a decrease in permeability at high flow rates. In contrast, flow-through experiments using cores with higher clay content result in little permeability change, as the mobilization of clays in the fracture counterbalances the increase in permeability due to the increase in fracture aperture.

The complexity of enhanced reactivity of fluid flow through faults and the dissolution/precipitation processes is better understood through natural analogues, such as the Colorado Plateau in Utah, which is a naturally leaky CO₂ reservoir. Extensive bleaching of the adjacent Entrada sandstone, mineralization of carbonates and celestine veins, and increased porosity in bleached sandstones are some of the observed alterations in multiple locations. The outcrops of bleached faults in Utah show that leaking faults can roughly be divided into three end-members based on the extent and type of leakage.

However, experiments need to be carried out under in-situ pressure and temperature conditions to allow the fault rock to compact if porosity-loss occurs. Advanced numerical models capable of resolving complex fracture geometries and representing flow, transport, reaction, and deformation processes are also required to make an accurate assessment of permeability changes in realistic fracture networks. The use of dimensionless numbers, such as Péclet and Damköhler numbers, can provide an insightful method to characterize the different dissolution regimes and identify the control factors among diffusion, advection, and chemical kinetics.

Finally, the authors concluded their study as below:

- 1. CO₂ injection can enhance flow in carbonate reservoirs, but may also cause channel collapse and decreased flow rates. Dimensionless numbers can provide insight, and models need to consider potential failure of high porosity zones.
- 2. Particle clogging and mineral precipitation can limit or decrease permeability in the vicinity of the injection well.
- 3. The effects of CO₂ on reservoir compaction vary depending on site-specific conditions, and any extrapolation from lab to reservoir scale should consider these effects.
- 4. Long-term mechanical impact of CO₂ on caprocks requires further research, with natural analogues and numerical models being valuable tools.
- 5. Formation of preferential flow channels in caprocks is less likely than in reservoirs, and additional experiments and models are needed to accurately assess permeability change in realistic fracture networks.
- 6. CO₂ may cause low-to-moderate shear strength weakening in shale/clay-rich and anhydriterich faults, but the effect on calcite-rich fault gouges is unknown (Rohmer et al., 2016).

2.6. Permeability variation at cyclic stress.

In underground gas storage (UGS), the multicycle gas injection and withdrawal causes a change in reservoir pressure, which can cause a change in the stress state of reservoirs. The mechanical properties of the reservoir rock may vary as a result of the stress disturbance, changing the rock's stress sensitivity, which in turn affects the reservoir's permeability and the effectiveness of the UGS. A lot of engineering has focused on the mechanical characteristics of rocks that are subject to cyclic stress. In the experimental study conducted by Zhou et al. (2023) is an interesting study that explores the effects of cyclic stress on the permeability of sandstone, and its implications for underground gas storage.

Researchers used a cylindrical sandstone sample from a gas reservoir for this study. X-ray diffraction was used to examine the sandstone's mineral makeup. The sandstone had low permeability, indicating it was a tight reservoir. Before testing, the sandstone was dried in an oven. The researchers conducted permeability and mechanical tests using a specialized system capable

of testing under complex stress paths and high-temperature high-pressure conditions. They measured the sandstone's permeability using the transient method with nitrogen. Simulating the stress variations that occur during cyclical gas injection and withdrawal in underground gas storage (UGS) was the goal. The sandstone sample was subjected to 50 cycles of controlled stress loading and unloading. At different gas pressures during each cycle, the researchers measured the sandstone's permeability to observe how it varied with gas pressure at each operation cycle.

However, there are also some limitations to the study. For example, the authors only use a single type of sandstone, which may not be representative of other types of sandstone that may be found in underground gas storage reservoirs. Additionally, the study only examines the effects of cyclic stress on permeability, and does not take into account other factors that may affect the behavior of sandstone under these conditions.

The experiments investigated the behavior of sandstone under cyclic stress and its effects on the stress-strain curve, elastic modulus (E), and Poisson's ratio (v) and demonstrated in Figure 3f.



Figure 3. The sandstone's stress-strain curves under cyclic stress (Zhou et al., 2023).

The following table summarizes the key findings:

Stress-Strain	•Hysteresis loops on the sandstone's stress-strain curve indicated irreversible
Curve	inelastic deformation upon stress unloading.

	• The hysteresis loops shifted towards the strain-increasing direction and
	became denser with increasing cycles, suggesting a decrease in irreversible
	deformation.
	• The sandstone primarily showed elastic deformation under cyclic stress, with
	limited plastic deformation.
	•This behavior was attributed to the closure or expansion of pores and
	microcracks during cyclic stress loading and unloading. The plastic
	deformation rate decreased with the number of cycles.
	• The E of the sandstone initially increased rapidly in the first 20 cycles, then
	slightly decreased between the 20th and 30th cycles, and finally remained
	almost constant between the 30th and 50th cycles.
	• The change in E was closely related to crack initiation, propagation, and
	coalescence.
	• In the initial cycles, the preexisting pores and fractures in the sandstone
Elastic	underwent continuous compaction, leading to an increase in E.
Modulus (E):	•Between the 20th and 30th cycles, new microcracks formed due to fatigue
	damage, resulting in a slight decrease in E.
	• In the last 30-50 cycles, the microcracks in the sandstone were completely
	compressed, causing E to stabilize.
	•Overall, the deformation behavior of the sandstone was predominantly
	influenced by compaction in pre-existing pores and cracks due to relatively
	lower deviatoric stress levels.
	• The sandstone's Poisson's ratio (v) initially grew over the early cycles before
	essentially remaining steady.
Poisson's	• In the early cycles, the preexisting pores and fractures underwent rapid
Ratio (v)	compaction, leading to an increase in v .
	• With increasing cycles, the sandstone primarily exhibited elastic deformation,
	resulting in no significant change in v.

Table 2. The mechanical properties of sandstone under cyclic stress

These findings show that the mechanical behaviour of sandstone is affected by cyclic stress loading and unloading, with the sandstone mostly displaying elastic deformation and minor plastic deformation. The deformation response is significantly influenced by the compaction of preexisting pores and fissures, which alters the sandstone's stress-strain curve, elastic modulus, and Poisson's ratio.

The experiments focused on studying the evolution of permeability in sandstone under different gas pressures and deviatoric stress cycles has been provided in the table below:

	For each stress cycle, the permeability of the sandstone at the maximum stress was lower
1.	than that at the minimum stress. This is because higher deviatoric stress leads to more
	significant compression of pore spaces, reducing the permeability.
	The permeability of the sandstone decreased with increasing cycles and three steps can be
	distinguished:
	I. Rapidly decreasing stage (1-10th cycles) – The permeability significantly decreased due
	to irreversible deformation from cyclic stress loading and unloading. Compression of
n	pores and fractures narrowed flow channels, leading to a sharp decline in permeability.
۷.	II. Slightly decreasing stage (10-30th cycles) – Pore and fracture compression continued
	but at a slower rate, resulting in a slower decline in permeability compared to before.
	III. Almost stable stage (30-50th cycles): Plastic deformation weakened, reducing fatigue-
	induced microcracks and compacting pre-existing and newly formed microcracks. This
	stability led to almost constant permeability during the stress cycles.
	Figure 4 demonstrates that, as the pressure of the gas injection rose, the sandstone's
3.	permeability rose. This is because rock permeability generally inversely correlates with
	effective stress. Therefore, higher gas injection pressure reduced effective stress, leading
	to increased permeability in the sandstone.

Table 3. The permeability evolution of the sandstone sample subjected to cyclic stress.



Figure 4. The sandstone's permeability changed as a result of different gas injection cycles at varied pressures (Zhou et al., 2023).

These findings highlight the importance of understanding the dynamic variation of permeability in sandstone during procedures of subsurface gas storage. Permeability directly impacts gas injectivity and productivity, as well as gas storage capacity evaluation.

The results showed that the permeability of the sandstone was highly dependent on stress. As the cycles increased, the permeability decreased, and the rate of permeability change corresponding to effective stress decreased. This suggests that the influence of stress perturbations on permeability weakened with increasing cycles during gas injection or withdrawal processes.

It was observed that the permeability of the sandstone did not fully recover to its initial state at the end of the cycles. The irreversible permeability loss rate (IPLR) of the sandstone increased gradually with cycles. At a given cycle, the IPLR was higher at the maximum stress compared to the minimum stress. For example, after the 10th cycle, the IPLR at different gas pressures ranged from 3% to 41% at the minimum stress, and from 5% to 40% at the maximum stress.

The IPLR continued to increase with cycles. After the 50th cycle, the IPLR ranged from 4% to 55% at the minimum stress and from 8% to 55% at the maximum stress, depending on the gas pressure. The evolution of IPLR with cycles corresponded to the variation of the stress sensitivity coefficient and the alteration of rock mechanical properties due to cyclic stress loading-unloading.

The pore space compaction in the sandstone caused the irreversible permeability loss primarily in the early cycles. However, as the cycles progressed and the pore space became more compressed, the rate of permeability loss slowed down (Zhou et al., 2023).

2.7. Injection-induced stress, strain and microseismicity.

Initial attention to geomechanics in geologic carbon storage (GCS) began in the late 1990s, and recent studies have shown substantial geomechanical modifications associated with CO_2 injection at real-world sites. Concerns have arisen about the possibility of triggering seismic events, which could impact the integrity of CO_2 repositories and public perception of GCS. Public concerns have already led to the suspension of some GCS projects. Hence, large-scale GCS must be developed with caution, and geomechanics will play a crucial role in analyzing site-specific risks to ensure safe operation.

In a study conducted by Rudqvist (2012), an examination was carried out on the geomechanics and modeling aspects of geologic carbon storage (GCS), specifically targeting the storage in deep sedimentary formations, particularly saline aquifers. The notion of storage in deep sedimentary formations, associated geomechanical processes and problems, and pertinent geomechanical modelling techniques are initially introduced in the study. The analysis of geomechanical elements is then more in-depth and covers topics like reservoir microseismicity and stress-strain, caprock sealing performance, well integrity, and the likelihood of fault reactivation and noteworthy seismic events.

The important geomechanical processes that identified by the author are as below:

- Stress-and-strain changes Reservoir pressure and temperature changes induce changes of stress-and-strain in and around the injection zone, which lead to changes in permeability and injectivity and also ground surface deformations.
- Microseismic events The injection-induced increase in fluid pressure and deformation of both the reservoir and the surrounding rock have the potential to induce minor seismic events. These events can be triggered by various factors, including in situ stress conditions, injection pressure, presence of fractures, and properties of the rock formation.
- 3. Mechanical changes at high pressure As the reservoir pressure reaches a critical threshold, significant and irreversible mechanical alterations can take place. These changes involve straining of the well assembly, the formation of new fractures, and the reactivation of larger faults located within the reservoir, caprock, or overburden layers.
- Increased upward migration driven by buoyancy The mechanical alterations have the potential to create new flow paths in low-permeability cap formations, facilitating an enhanced, buoyancy-driven upward movement of the injected CO₂.

Also, the author mentions that there are some technical issues that can occur during GCS which are:

- 1. Ground-surface uplift Geomechanical changes can cause Observable ground surface deformations, which need to be monitored.
- 2. Permeability and injectivity changes: Geomechanical changes can result in noticeable alterations in permeability and injectivity, affecting the efficiency of CO₂ injection and storage.
- 3. Microseismic monitoring Monitoring microseismic events is crucial as they offer valuable insights into geomechanical processes and subsurface fluid flow.
- Significant seismic events Reactivation of faults or creation of new fractures can potentially cause significant seismic events, which may raise concerns in local communities and need to be assessed.
- 5. Hindering the upward migration: The existence of multiple low-permeability layers in the overburden plays a vital role in hindering the upward migration of CO₂, even if faults are reactivated within the injection zone.
- Risk assessment: Geomechanics plays a main role in assessing the suitability of an injection site and determining risks such as significant seismic events, CO₂ release to shallow aquifers or the surface, and leaky wells or faults.



Figure 5. Geomechanical processes and critical technical challenges related to GCS (Rutqvist, The geomechanics of CO2 storage in deep sedimentary formations., 2012).

In the Figure 5, the upper part depicts the various areas where a CO_2 plume can have an impact, including reservoir pressure alterations and geomechanical shifts in a system composed of multiple layers with both minor as well as major faults. The lower left section depicts the effects of injection-induced changes in reservoir pressure and temperature, including strain, stress, deformations, and potential occurrences of microseismic events. The lower right section represents undesired irreversible alterations that could decrease the effectiveness of CO_2 sequestration and raise concerns within the nearby community.

The research mentions that numerical simulators combining fluid flow and geomechanics are being used to analyze geomechanical issues in Geological Carbon Storage (GCS). These simulators can handle multiphase flow and transport of CO₂ and brine, and some also incorporate geochemistry. Several examples of such simulators are mentioned, including TOUGH-FLAC, FEMH, OpenGeoSys, CODE-BRIGHT, ECLIPSE-VISAGE, STARS, NUFT-SYNEF, DYNAFLOW, and others that combine multiphase flow codes like ECLIPSE, TOUGH2, and GEM with geomechanical codes. However, they require numerous input parameters, and simplified models can be sufficient for specific studies. For fast evaluations of the suitability of a CO₂ injection site, analytical models and numerical flow models connected to analytical geomechanical models are helpful. The review also incorporates geomechanical observations from a few of the GCS field deployments. The CO_2 storage project in Salah is one of them. CO_2 is introduced into a relatively thin and compact sandstone deposit at an injection overpressure that is much higher than the initial formation pressure. This area has seen geomechanical changes brought on by injection, and these changes play a crucial role in the field monitoring programme.

The paper discusses how injection of fluids into a reservoir can cause changes in the stress field and lead to ground surface deformation. Based on the findings of researcher it is possible to say that the magnitude of the uplift is proportional to the pressure increase and depends on the geomechanical properties of the reservoir and surrounding sediments. The search provides examples of CO₂ injection causing ground surface deformation in the CO₂ storage project. It also highlights the use of Interferometric Synthetic Aperture Radar (InSAR) to detect ground surface deformation and the importance of favorable ground surface conditions for high-resolution InSAR data.

Given the shallow sandstone deposit being injected into at a depth of about 2 kilometres, the comparatively minor elevation seen above the In Salah CO₂ injection wells may appear unexpected. However, such an uplift can be estimated using straightforward mathematical procedures. The author calculated the uplift as a 3 cm vertical expansion using a formula from Fjaer et al. (2008) and values from Rutqvist et al. (2010). The searcher cautions that the utilised equation is only a rough approximation because it uses a 1-dimensional uplift model that may overstate the uplift and assumes that changes in well pressure extend uniformly across a wide area.

The results of two research have been discussed: one on coupled numerical modelling by Rutqvist et al. (2010) and one on inverse semi-analytical deformation analysis by Vasco et al. (2008a, b). These investigations investigate the relationship between the uplift seen at the In Salah CO2-injection wells and the expansion straining caused by pressure at the injection depth.

The findings of two investigations that look into what causes uplift at CO₂-injection wells one by Vasco et al. and the other by Rutqvist et al.—are discussed in the study. According to the investigations, expansive straining brought on by pressure at the injection depth in the rock formations can account for the observed elevation.



Figure 6. After three years of injection, the injector's vertical displacement and the fluid pressure of reservoir around injector (Rutqvist et al. 2011b)

The calculations show that pressure-induced elastic expansion inside the 20 m thick injection zone can account for the observed uplift at the injection wells. Reservoir pressure changes, which are more extensive laterally than the CO_2 plume, are the main cause of the uplift. The uplift is constrained by the overburden's stiffness, resulting in a vertical displacement of around 1.6 cm at the top of the injection zone and 1.2 cm at the ground's surface (Figure 6). After 2.5 years of injection, this amount of uplift is consistent with the data collected at the KB-501 injection well. According to these results, the injected CO_2 and displaced brine remained at depths of around 1.8 to 1.9 km inside the storage unit that was designed for them.

While the horizontal stress changes as a result of poroelastic stress during injection, the vertical stress remains largely constant. The geometry and poroelastic characteristics of the reservoir-caprock system influence the changes in horizontal stress caused by injection. The author hypothesised that the total horizontal stress would rise by a factor of 0.75 of the fluid pressure change in accordance with the equation given by Hawkes et al. (2005).

Results from numerical simulations were utilised in Rutqvist et al. (2011a) to calculate the likelihood of injection-induced microseismicity at In Salah. Calculations of the effects of injection, taking into account the fractures inside the injection zone, were made. The possibility of shear slip reactivation along existing fractures and related generated microseismicity were assessed using a Mohr-Coulomb failure criterion. It was discovered that the fractures within the injection zone were sub-vertical, primarily hitting NW-SE and parallel to the direction of the maximal primary stress. With the help of the maximum compressive horizontal effective stress, the critical stress for shear failure, and the minimum compressive horizontal effective stress, a straightforward criterion for

the onset of shear slip was developed. The injection-induced cooling and pressure increase near the injection well was predicted to have the highest potential for induced microseismic occurrences.

In comparison to earlier studies, updated results indicated a somewhat increased probability for microseismic occurrences. The simulation's findings suggested the possibility of generated seismicity because calculated shear stress was greater than the shear strength of fractures around the wellbore that were optimally aligned. According to preliminary microseismic monitoring, there were some microseismic occurrences going on that might be related to the injection rate. The potential for induced seismicity was estimated using straightforward analytical analysis, and the findings of the numerical simulation were compared with it. Prior to and during injection, the strength-to-stress margin was calculated while accounting for fluid pressure, stress alterations brought on by cooling shrinkage, and thermal stress. The simulation results may be trusted because the estimated strength-to-stress margin (-1.7 MPa) matched the numerically computed values close to the injection well.

The possibility for induced microseismic occurrences close to the injection well due to stress changes brought on by injection is highlighted by these findings. They also emphasise the value of combining numerical simulation with monitoring data to gain a better understanding of geomechanical processes.

The paper also discusses the monitoring and analysis of seismic activity related to CO₂ injection projects at various locations, including the Otway project, Weyburn, and the Aneth oil field. The monitoring efforts reveal minimal seismicity, typically, the frequency of events is fewer than five per day, and their magnitudes generally fall below zero. There is no clear connection between seismic activity and injection pressure history. In Weyburn, microseismicity has been monitored since 2003, with fewer than 100 recorded events, indicating a low rate of seismic activity. Many of these occurrences take place outside the injection zone in the overburden and are brought on by stress transfer brought on by reservoir expansion. Since 2008, many microseismic events have been recorded in the Aneth instance, defining fracture zones on opposing sides of the reservoir. Microseismic activity variations may be brought on by stress changes brought on by longer-lasting production or injection. Weyburn and Aneth's findings suggest that geomechanical changes can take place outside the injection zone. The production of hydrocarbons has also been associated with microseismic activity. However, all recorded injection-induced microseismic events thus far have been small and detectable only through geophones. The presence of a fracture

network, relating to areas of cracked rock or fault damage, allows for the reactivation or merging of smaller fractures. Larger seismic events would necessitate a larger fault-rupture area. Additionally, chemically mediated compaction may occur in carbonate-rich reservoirs exposed to CO₂, resulting in increased dissolution of minerals, mechanical weakening, and enhanced compaction creep. Laboratory studies have demonstrated these effects on rock samples, particularly in carbonate-rich rocks. Such effects can influence the stress evolution within the reservoir, surrounding rocks, and overburden, potentially leading to irreversible subsidence.

The research has covered the significance of caprock sealing qualities in the storage of gas, notably CO_2 , in gas and oil reservoirs and saline aquifers. In the study, the need of having an appropriate caprock is emphasised. This caprock should be made of thick layers of fault-free clays, claystones, mudstones, salt beds, or evaporates. To stop CO_2 from migrating upward, the caprock needs to have a high capillary entrance pressure, low permeability, and be homogeneous over a sizable area.

The article discusses the importance of caprock effectiveness and highlights potential issues, including gas leaks and pressure-triggered leakage mechanisms. Fractures and faults within the caprock are emphasized for their impact on capillary entry pressure reduction and increased permeability. This can result in a breach in the top seal, enabling the flow of CO₂ in a Darcy type manner. The presence of faults and fractures plays a vital role in determining the sealing capacity of the caprock, making it crucial to monitor microseismicity and surface deformations for early detection of geomechanical changes.

Also covered is the effect of chemical-mechanical coupled processes on the effectiveness of caprock sealing. Studies indicate that these processes have a negligible effect on mudstone or shales caprocks, with CO₂-rich fluid perhaps only having an impact on the lowest few metres. In carbonate-rich rock, however, problems like CO₂-induced shrinkage and mineral dissolution may manifest, particularly along faults and fractures produced by high CO₂ injection pressure.

The significance of caprock characteristics in the storage of gases, particularly CO_2 , in oil and gas reservoirs and saline aquifers is also covered in the study. It emphasises the necessity of an appropriate caprock that serves as a seal to stop gas migration. A uniform layer thickness of clay, claystone, mudstone, evaporates, or salt beds should make up the perfect caprock. Laboratory experiments are used to assess the capillary entrance pressure, which determines the capillary seal against upward CO_2 migration. This pressure can range from less than 0.1 MPa to 10 MPa. The caprock may operate as a permeability barrier if the CO₂ overpressure is greater than the capillary entry pressure, however fracturing or opening of cracks and faults due to high injection pressure can weaken the seal. Pre-existing faults and fractures within the caprock can affect its sealing capacity, and the mechanical properties of the caprock units play a crucial role. Geomechanical monitoring is important for detecting potential geomechanical changes, such as fault reactivation. Caprock sealing performance may be slightly influenced by chemical-mechanical processes, but the potential for CO₂-induced shrinkage or mineral dissolution exists. Overall, understanding and monitoring caprock properties are essential for effective gas storage (Rutqvist, The geomechanics of CO2 storage in deep sedimentary formations., 2012).



Figure 7. The importance of preserving top seal integrity to prevent hydrocarbon buildup, based on Ingram et al.'s findings (1997). Capillary seal: Sealing occurs at the CO2-water interface, preserving a distinct pressure difference. Permeable seal: CO2 infiltrates the seal, maintaining a pressure gradient. Hydrofracture: High CO2 pressure can exceed fracture strength, resulting in leakage by means of fractures. Bottom: Fault-related leak path. Small faults can connect leaky strata in the top seal, forming complex but effective leakage pathways over time (Rutqvist, The geomechanics of CO2 storage in deep sedimentary formations., 2012).

2.8. The geomechanical reactions of reservoirs caused by GCS

The intricacy and ambiguities surrounding the sequestration of CO_2 as a strategy for lowering greenhouse gas concentrations in the atmosphere are discussed in a study by Eshiet and Sheng (2014). The research focuses on comprehending the difficulties in making precise forecasts because there are so many variables and interactions at play. The authors stress the importance of taking into account several factors to successfully navigate the intricacies of the process, despite the fact that CO_2 sequestration has the ability to reduce climate change and delivers economic benefits like better oil and gas recovery. The paper examines many subsurface processes that should be included in models for more accurate predictions, including hydrogeological, geochemical, and geomechanical processes.

The authors refer to numerous research that have examined particular CO_2 storage-related consequences and aspects, such as geochemical effects, hydrogeological systems, and geomechanical behaviour. Due to the enormity of the issue and the demand for long-term forecasts, they also stress the significance of computational analyses. In this study, a novel method for analysing fluid-solid mechanical effects at the microscale and scaling them up to field size phenomena is presented. In this method, the controls affecting fracture propagation during CO_2 injection and pressure buildup in various rock formations are investigated. Other numerical approaches are criticised by the authors for their shortcomings in simulating geomechanical processes, such as their reliance on continuum formulations and insufficient treatment of fluctuations in porosity and permeability brought on by failure. They contend that by offering more precise and dynamic models of fracture initiation and propagation, the DEM technique enhances the accuracy of forecasts for geoenvironmental systems.

A particle flow model was employed in the study. Rigid particles make up the model, and they only communicate with one another at interfaces or points of contact. These particles differ from the traditional concept of particles in solid mechanics in that they occupy a defined space and have independent motion.

The model was sized to represent a field, and CO_2 was injected using an injection well. The model has 20 m × 20 m of overall geometric dimensions, a well with a diameter of 0.5 m, and one perforation channel at the bottomhole where CO_2 is introduced. The models for heterogeneous rock materials with stratified layers and homogeneous rock materials with non-uniform particle sizes are also explored. The layers of the heterogeneous models are arranged in increasing, decreasing,

or alternating patterns and have different strengths. To study how fluid pressure disturbance affects faults, stratified models incorporate a fault line that symbolises a zone of weakness.

All types of materials utilised to calibrate the microscopic mechanical properties before calibrating the fluid flow properties underwent biaxial tests. The results of the biaxial tests are then utilised to choose appropriate microscopic parameters for the DEM model, such as contact-bond strength and particle stiffness. These parameters are changed to reflect the physical characteristics and macroscopic characteristics of real rocks.

To generate a sufficiently large model while maintaining numerical and computational stability, the scientists picked particle sizes for generating particle assemblies that were larger than actual rock grains. Additionally, the scientists looked into how particle size affected important strength (compressive strength) and deformability (elastic modulus and Poisson's ratio) characteristics:





Table 4. the main characteristics of strength and deformability.

The behaviour of fluid injection and its effect on fracturing patterns were examined by the authors using simulations. Three instances were investigated. The first case involved injecting fluid into a homogenous formation through a cased well. In the second and third occurrences, different rock layer characteristics were present in layered formations. The table below displays the simulation results.

Case	Results and Findings
Homogeneous Formation CO2 is injected into a cased well in a homogeneous reservoir formation. When it comes to the mechanical properties of a material, differences in particle size and distribution are not addressed.	The process starts with tension-induced cracks, followed by shear fractures. As fluid application continues, shear failures become more common. Fracturing is influenced by initial and boundary stress conditions. Upper well section fracturing is caused by confining stresses, well geometry, and rock strength. Fluid pressures and reservoir pressure changes affect the stress field, leading to fracturing propagation in the direction of fluid pressure and weakened strength (Figure 8a).
Stratified Formation: Increasing Strength Injection of CO2 into a stratified, heterogeneous reservoir formation. Rock layers are organised according to increasing strength going deeper. The injection duration is equal to that in the homogeneous scenario.	Fracturing pattern around injection point is like homogeneous formation. Fractures that extend to higher layers are shown to grow further. High magnitudes of stresses are produced by fluid pressure at the injection spot. The fracturing inclination aligns with the direction of fluid pressure propagation and decreasing strength. Injection processes have the potential to impact faults or vulnerable zones located in distant regions (Figure 8b).
Stratified Formation: Decreasing Strength The only difference from the previous stratified formation case is that layers are organised in the order of decreasing strength going deeper.	A similar fracturing pattern was observed at injection point. The fracturing inclination aligns with the direction of fluid pressure propagation and decreasing strength, so it grows downward. Tensile failures brought on by drag forces in high-pressure disturbance zones were preceded by the formation of cavities. Low permeability, low density, and low bulk modulus of the host rock and fluid are the causes of slow fluid flow (Figure 8c).

Table 5. Cases studied and simulation results.



Figure 8. Fracture development at the end of the injection period: a) homogeneous formation; b) stratified formation: increasing strength; c) stratified formation: decreasing strength.

When comparing the three cases, it becomes evident that all three had a tendency to fracture typically in the trajectory of fluid pressure propagation. In the three reservoir formations, the evolution of crack demography, including the creation of tensile and shear cracks, followed identical patterns. However, shear failures became more pronounced in areas of lower strength, and the existence of stratification and changes in rock strength affected the extent and trajectory of fracture propagation (Eshiet & Sheng, 2014).

2.9. Mechanical effects due to CO_2 exposure of caprock

Caprock is crucial to maintaining the containment of the storage reservoir. The caprock, which is typically composed of shale formations, may experience considerable stress oscillations and associated changes in undrained pore pressure, especially close to wells and faults that border the reservoir. It might also come into touch with various brine and CO₂ solutions. Therefore, it is necessary to precisely assess the mechanical properties of these shale formations which are

positioned on top of the storage reservoir, both in their initial state and after being exposed to various CO₂ solutions.

In the paper by Cerasi et al. (2022) different laboratory tests which conducted on plugs obtained from the Draupne shale formation in the Ling Depression from the North Sea.

Small specimens were subjected to triaxial testing, specifically consolidated isotropic undrained tests (CIU) and unconfined compression strength tests (UCS) under confining stresses of 10 and 15 MPa. The test samples used were cylindrical plugs. The plugs had a diameter of 15 mm and a length of 30 mm. For studies involving fluid substitution, larger samples with measurements of 1" in diameter by 2" in length (25.4 cm x 50.8 cm) were also made.

Using a low-frequency rig, a non-destructive stiffness test with the presence of CO_2 was performed. Repetition of cyclic stiffness measurements and pore fluid exchange were part of this test. The specimens for the test were cylindrical plugs with 1" diameter and 2" length. The test involved three phases: consolidation phase with no fluid flow, exposure to brine with a flow rate of 0.025 mL/min, and exposure to supercritical CO_2 dissolved in brine at the same flow rate.

On thin discs of Draupne shale, shear strength measurements were made using the PUNCH technique. To evaluate the shear strength, a method of drilling holes into the shale discs was used. The dimensions of the discs were 15 mm in diameter and 3 mm in thickness. The exposure tests considered 6 distinct fluids: brine, CO_2 gas dissolved in brine, supercritical CO_2 (sc CO_2) dissolved in brine, dry gaseous CO_2 , dry sc CO_2 , and room-temperature air.

Tests	Comparison of the results after changing from brine to CO2-saturated brine
Triaxial tests	Poisson's ratio decreased from 0.3 to 0.2
	Young's modulus decreased from 4.5 GPa to 4.2 Gpa.
	Skempton B coefficient dropped from 0.5 to 0.3.
	UCS increased from 23 MPa to 29 MPa.
Low-frequency	Stiffness: while brine exposure caused a drop in stiffness, scCO ₂ -brine caused a
stiffness tests	slight increase. However, the magnitude is small, and the impacts are considered
	as negligible.
Shear strength	No significant variation observed in strength.
measurements	

Table 6. The results of the three different tests.

The tests conducted did not show any significant weakening when exposed to CO₂-saturated brine compared to regular brine. This suggests that the strength of the cap rock is not compromised

by CO_2 exposure. However, it is important to note that slow diffusion of CO_2 into the cap rock could still lead to changes in the mechanical properties of the overburden pore fluid. These changes can affect the poroelastic parameters of the rocks, such as Skempton B parameter, and subsequently impact the magnitude of undrained pore pressure changes due to various stress state alterations (Cerasi et al., 2022).

2.10. On sorption and swelling of CO_2 in clays.

The clay minerals found in shales, particularly swelling clays like montmorillonite (MMT), can interact with CO₂ due to its distinct wetting behaviour. The effectiveness of caprocks and wells as sealants can be affected physically by CO₂-clay interactions under realistic reservoir conditions. For effective geological storage of CO₂, understanding these interactions is crucial.

In their study, (Busch et al., 2008) investigated the physical adsorption of CO_2 at high pressures and temperatures on shale and clay samples. The findings demonstrated that whereas chlorite adsorbed very little CO_2 , clay minerals, in particular Ca-exchanged smectite, absorbed substantial amounts. Clays' ability to sorb water was shown to be lowered by the presence of water.

In their 2016 study, A. Busch et al. compiles the measured maximum excess CO_2 adsorption capacities and specific surface areas (SSA) for various clays, shales, and activated carbon materials. In terms of excess CO_2 sorption versus N_2 BET area (the specific surface area obtained using the Brunauer-Emmett-Teller (BET) method with nitrogen (N_2) gas adsorption), it has been discovered that clays, mudrocks, siltstones, and activated carbon follow a power law function. The presence of ultramicro pores in natural coals, on the other hand, consistently results in increased adsorption capabilities. The authors contend that supermicropores, mesopores, and macropores are where sorption in clays and mudrocks takes place, while ultramicropores are where CO_2 is largely adsorbed in coal samples (Busch et al., 2016).

The excess sorption of CO_2 in clays and other materials decreases after a maximum point, occasionally even turning negative at high fluid densities. This maximal sorption happens at pressures that are lower than those used to store CO_2 . With positive values indicating denser sorption phases, negative values showing more effective storage in the bulk pore volume, and zero excess sorption indicating equal densities of both phases, excess sorption reflects the advantage of adsorbing CO_2 over storing it in the bulk phase. In a study on montmorillonite, the density of the

sorbed phase is investigated. The results show that the sorbed CO₂ density is initially greater and eventually reaches gas density at 8–10 MPa. Negative excess sorption results from further pressure rises. Other research have shown corresponding tendencies. Weakly attractive fluid-solid interactions, which favour fluid-solid interactions at low densities and fluid-fluid interactions at high densities, cause high-density interfacial fluid depletion (Rother et al., 2013).

An analysis of tests assessing the swelling strain of various clay minerals, specifically smectite samples with different cations (K, Ca, and Na), using X-ray diffraction is presented in a research by (Busch et al., 2016). The Source Clays Repository's standard clay sample was used for the measurements. The outcomes demonstrated that the clay's initial interlayer spacing and degree of hydration have an impact on the swelling strain.



Figure 9. Summary of the maximum smectite interlayer spacing d_{001} following charging the samples with CO₂. Water layers found between layers are related to hydration states (0, 1 W, etc.). Data from Giesting et al. (2012a, b), Rother et al. (2013a), Schaef et al. (2012), de Jong et al. (2014).

Swelling strain was not detectable in dry smectite with a narrow interlayer spacing or in nonexpandable clays like illite. However, when the hydration state grew towards one water layer (1 W), smectite containing modest amounts of water demonstrated a considerable rise in swelling strain. The swelling strain returned to values close to zero at hydration levels close to 1 W. Shrinkage of the interlayer spacing was noticed in higher hydration states corresponding to shallow burial depths, indicating water loss from the sample, presumably as a result of water dissolving in CO_2 (Figure 9).

The interlayer cation was also discovered to be important for the swelling strain. Similar swelling strains were seen in the Na and K exchanged samples, which returned to their initial values

at distinct water layers. The swelling strains in the Ca-exchanged samples were greater, and they only reverted to their initial values at a 2 W hydration state.

For subsurface applications, it is essential to understand the hydration condition at various depths; however, the precise hydration states of clay in geologic reservoirs are uncertain. Though CO₂ trapping varies among research, speculative models suggest a persistent carbonate species in the clay interlayer may explain swelling behaviour.

Further research has revealed that the ability of interlayer CO₂ absorption is dependent on water content. When moving from the 0 to 1 W hydration state, CO₂ concentration rises sharply; however, as water content rises, interlayer CO₂ concentration falls and reduces at the 2 W hydration state. Recent research utilising a variety of methods have confirmed clay swelling between 0 and 2 W hydration states. The interlayer spacing does, however, begin to contract for hydration states beyond 2 W, most likely as a result of dry supercritical CO₂ removing water under conditions close to the surface.

In order to ascertain the swelling stresses brought on by CO₂ sorption in Na-exchanged Wyoming smectite clay, Zhang et al. (2014) conducted experiments. Under various hydration levels, effective stress conditions, and temperatures, they measured isovolumetric swelling stresses ranging from 30 to 80 MPa. Lower stresses were seen in control studies employing inert gases or non-swelling clays. These swelling stress values were utilised by Wentinck and Busch (2014) to compute the shear capacity utilisation (SCU) in several reservoir situations. They discovered that reservoirs with high swelling clay content are more susceptible to shear collapse over very long time scales. The potential for shear failure and the development of large swelling stresses are influenced by a number of variables, including the amount of clay present, the stress environment, the rate of CO₂ penetration, and the stress relaxation. Further investigation is necessary, particularly in regards to fault behaviour and stress changes brought on by clay swelling, as the creation of a permeable route after shear failure is uncertain.

To interpret experimental findings regarding CO_2 storage in clay minerals, various molecular dynamics (MD) simulation studies were carried out. The purpose of the experiments is to comprehend how CO_2 molecules behave as they penetrate hydrated clay interlayers and how this affects the strain response. Recent MD investigations using density functional theory have shown that CO_2 can intercalate the clay mineral interlayer, leading to a positive strain (Cygan et al. 2012; Myshakin et al. 2013, 2014; Spiering et al. 2014). The early clay hydration state affects the strain's strength. These simulations mostly took place in reservoir settings, simulating supercritical CO_2 . Studies have shown that swelling rises when water and CO_2 molecules per unit cell increase. Although there are still significant differences, different initial water/ CO_2 ratios can result in stable final states, supporting the experimental findings.



Figure 10. Various CO₂ interactions with clay minerals causing sorption (for all clays) and swelling (only for smectite) (Busch et al., 2016).

The consequences of the CO₂/clay interaction on CO₂ trapping in the reservoir and probable leakage channels such wellbores, faults, fractures, and the caprock's capillary network are the main focus of the study by (Busch et al., 2016). The writers talk about several situations, such as direct leaking and clay minerals enhancing storage capacity. To comprehend the potential advantages and dangers involved, they investigate the mechanics and limitations of clay sorption and swelling (Figure 10).

The sorption of CO_2 on clay material surfaces in reservoirs was investigated by the authors. They used a variety of analytical techniques to examine the surface areas of several clay minerals, notably kaolinite, illite, chlorite, and smectite, in order to explore their physical sorption capacities. They also looked at the significance of clays' capacity to capture CO_2 in carbon dioxide storage reservoirs. Their research's conclusions include:

- Compared to other prevalent reservoir rock minerals like quartz and feldspar, clay minerals have much larger surface areas. With smectite having the highest values, the reported surface areas for various clay minerals range from 5 to 120 m²/g.
- 2. The authors assessed the clay content, which ranged from 3% to 8% in the various CO₂ storage reservoirs described in the literature. They computed the relevance of CO₂ trapping by sorption in a simplified instance using this information. In their calculations, which took into account equilibrium conditions and particular mineralogical compositions, residual/structural trapping emerged as the predominant process, followed by sorptive trapping and dissolution.
- 3. They observed that structural trapping and sorption are complimentary processes taking place in the same pore regions. The amount of pore space that is filled by the sorbed phase reduces the amount of space that is open to bulk CO₂. If the density of the sorbed phase is higher than that of the bulk CO₂, this aids in trapping and boosts the total storage capacity.
- 4. The sorbed layer has a lower average density than the bulk CO₂, according to experiments that have showed negative excess sorption capacity at high pressures, as the authors noted. In reservoirs with negative excess sorption capacity, this means that the same amount of fluid in the sorbed layer occupies a larger volume than the bulk, resulting in higher pressures.

The interaction between CO_2 and clay minerals at the interface of a reservoir seal is the subject of the following case study. Due to its buoyancy, CO_2 rises towards the reservoir/seal contact after being injected into storage reservoirs. Under the seal, a column of CO_2 develops, resulting in a differential pressure across the contact. CO_2 may seep into the mudrock's capillary network if this pressure is higher than the seal's capillary entry pressure.

The wettability and interfacial tension between water and CO_2 determine the capillary entry pressure. Capillary entry pressure is difficult to forecast for mudrocks with limited permeability. Diffusion becomes the predominant transport method if the buoyancy of CO_2 does not exceed the seal entry pressure. From the reservoir/caprock contact to the top of the shale package, concentration gradients induce diffusion.

The diffusion of CO_2 through a shale package is examined by the model of (Busch et al., 2008) that is detailed in the study. It takes into account CO_2 sorption on clay minerals and concentration gradients. The findings indicate that CO_2 breakthrough happens sooner than the regulation threshold of 10,000 years, within a geological time frame of about 50,000 to 70,000 years.

Following breakthrough, CO₂ sorption on clay minerals improves flow rates and aids in the considerable immobilisation of CO₂. This immobilisation lowers reservoir pressure and increases storage safety. According to the model, CO₂ sorption and diffusion in shale formations have a low effect on storage capacity and containment and give a promising long-term storage potential.

Shear failure in connection to CO_2 storage and its interaction with clay-rich caprocks was studied by the authors. Depending on the current stress conditions, pre-existing flaws may reignite. Faults are critically stressed when the stress condition meets the Coulomb faulting requirement. An essential consideration is how the fault is oriented in relation to the direction of highest stress. The authors note that CO_2 has a negligible impact on fault friction characteristics, suggesting that only highly stressed faults can slip during CO_2 storage. Additionally, permeable faults are the only ones that provide a danger of containment loss; mechanically active faults cannot become hydraulically active or permeable.

Wentinck and Busch (2014) conducted a numerical investigation on the possibility of sheartype collapse in a smectite-rich caprock surrounding a fault offset. The study made use of caprocks from the North Sea region with a 30% smectite content, which is normal. Aqueous diffusion, clay sorption, swelling stress and strain were all taken into account throughout the modelling process. According to the findings, swelling pressure has an impact on effective pressure, which could result in failure of the shear type. On a time scale of hundreds to thousands of years, a diffusional front is modelled as moving through the caprock and causing this collapse. Shear capacity can be exceeded if the front migrates far enough, and containment loss could happen if the failure leaves a permeable path.

However, there are a number of unknowns when estimating shear-type failure brought on by CO₂/clay interaction. According to variables like fluid composition, layer charge, and cation identity within the smectite interlayer gaps, swelling strain and stress evolve precisely. It is unclear how hydrated smectites are at various burial depths, and it is also unclear how swelling pressure builds up and decreases with time. It is still uncertain what thickness of caprock is required to

reactivate faults or form high permeability fractures. Furthermore, there is little knowledge of prospective flow rates, should fault permeability arise.

Fractures can also occur in geological storages. Both within a reservoir and across a seal unit, fractures are crucial passageways for fluid migration (Carey et al. 2015). Such channels may be impermeable due to self-sealing even if they are present, whether naturally occurring or created. CO₂ can bind to clay minerals on the fracture surfaces when it penetrates fractures in caprock or fault damage zones. The way the fractures were created affects how these clays align. Without taking into account chemical influences, clay swelling causes clay particles aligned parallel to the fracture surface to have smaller fracture apertures.

Potential leakage problems at the wellbore-seal interface are the study's last case. The authors attempted to explain how various elements, including the temperature difference between the CO_2 injection and production fluids, the contraction and expansion of the host rock and cement sheath, and the presence of an annulus with a diameter of a few micrometres between the host rock and cement, can all affect the formation of leakage pathways.

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The study includes calculations that take into account the CO_2 and water diffusional fluxes in the wellbore annulus. It implies that shale desiccation is likely to occur, and that the severity will depend on factors like the annulus aperture and diffusion coefficient. Shale desiccation can make the caprock more receptive to CO_2 , which will have an impact on sorption, swelling, and shrinking. The shale's expanding clays may cause CO_2 to be absorbed, to swell, and to put swelling stress on the formation. Even though it is doubtful that stability problems will actually arise since the well is cased during CO_2 injection, this may have ramifications for wellbore stability. However, additional negative consequences including volumetric expansion and changes in fluid pressure might be more likely as a result of mudrock swelling (Busch et al., 2016).

3. Conclusion

In conclusion, the literature review has provided an insight into the various aspects of underground gas storage in rock formations, with a specific focus on CO_2 geological storage. The findings highlight the multifaceted nature of the interactions between CO_2 and reservoir rocks, caprocks, and clay minerals, and underscore the complexity involved in predicting and optimizing the performance of CO_2 storage projects.

One key aspect discussed is the impact of CO_2 on rock strength and mechanical properties. The reviewed studies demonstrate that CO_2 -brine activity can lead to a decrease in strength and elastic moduli while improving porosity and permeability. The duration of CO_2 residency in the rocks also plays a crucial role in the observed processes, with changes becoming evident early on and progressing over time. However, further research is needed to fully understand the impact of CO_2 on rock strength, necessitating comprehensive investigations through rock mechanical laboratory testing.

The alterations induced by CO_2 injection have been examined extensively, revealing changes in rock properties such as cement dissolution, deformations, and alterations in transport and elastic properties. These alterations are influenced by site-specific factors, including mineral composition, reactive minerals, and protective coatings. Field-scale tests, laboratory studies, natural analogue sites, and numerical models have all contributed valuable insights into these complex interactions. Numerical simulations, although limited in their scope, provide a means to study the coupling phenomena and assist in understanding the geomechanical responses.

The effects of CO_2 injection on chemically altered carbonates in storage projects have also been explored. The research highlights the impact on the reservoir and cap rock, affecting injectivity and integrity. Altered samples generally exhibit reduced failure strength and elastic moduli compared to intact samples. However, the understanding of chemical alteration processes remains challenging, and the need for advanced models that consider specific formation characteristics is emphasized. Different carbonate types exhibit varying susceptibility to chemical effects, further emphasizing the importance of site-specific factors for successful CO_2 geological storage.

The dissolution of CO_2 in pore fluids and its subsequent mechano-chemical interactions with rock minerals have been extensively studied. Laboratory experiments have provided valuable

insights into the alterations induced by CO₂, including changes in porosity, permeability, elastic moduli, and strength characteristics. However, it is crucial to consider site-specific conditions and the heterogeneities and dissolution regimes at reservoir scales for accurate assessments. The integrity of caprocks and fault zones is also vital for containment, with undamaged caprocks and properly sealed faults playing a crucial role in limiting CO₂ interaction. Ongoing research focuses on fault reactivation and its potential impact on storage projects.

The impact of cyclic stress loading and unloading on sandstone permeability for underground gas storage has been investigated. The findings indicate that higher stress levels lead to reduced permeability due to pore space compression, resulting in gradual irreversible permeability loss. Understanding the dynamics of permeability is crucial for optimizing gas storage operations.

Geomechanics is a crucial aspect of geologic carbon storage projects, as it impacts the integrity of CO_2 repositories and public perception. Various geomechanical processes, such as stress-and-strain changes, microseismic events, and mechanical changes at high pressure, highlight the complexity involved in these projects. Numerical simulators combining fluid flow and geomechanics provide valuable tools for analyzing and predicting geomechanical issues, but simplified models may also be useful for specific studies. Monitoring and analyzing seismic activity, surface deformations, and caprock sealing performance are essential for ensuring the safe operation of CO_2 storage projects.

The importance of considering hydrogeological, geochemical, and geomechanical processes in accurate predictions for CO_2 sequestration models is emphasized. The utilization of particle flow models and the exploration of different rock formations have enhanced our understanding of fracture propagation and fluid-solid mechanical effects. However, comprehensive computational analyses and dynamic models are required to enhance the accuracy of forecasts in geoenvironmental systems impacted by CO_2 sequestration.

Lastly, the interactions between CO_2 and clay minerals play a significant role in the effectiveness of caprocks and wells as sealants for CO_2 storage. The sorption and swelling behaviors of CO_2 in clays have been investigated, highlighting the advantages of adsorbing CO_2 over storing it in the bulk phase. The hydration state of clay minerals and the interlayer cation influence the extent of swelling. Molecular dynamics simulations and experimental studies have provided insights into the CO_2 /clay interactions and their impact on CO_2 trapping, diffusion, and storage safety. Additionally, potential risks such as shear failure, fault behavior, and leakage

pathways at the wellbore-seal interface have been examined, emphasizing the importance of considering CO_2 /clay interactions in the design and assessment of CO_2 storage systems.

In conclusion, this literature review underscores the complex nature of underground gas storage in rock formations and CO_2 geological storage. The findings highlight the need for multidisciplinary approaches, site-specific considerations, and advanced models to accurately assess and optimize CO_2 storage projects. Further research and comprehensive investigations are necessary to enhance our understanding of the interactions between CO_2 and reservoir rocks, caprocks, and clay minerals, and to ensure the long-term success and safety of CO_2 storage initiatives in the transition to a low-carbon economy.

4. References

- Bemer, E., & Lombard, J. M. (2010). From injectivity to integrity studies of CO2 geological storage-chemical alteration effects on carbonates petrophysical and geomechanical properties. Oil & Gas Science and Technology–Revue de l'Institut Français du Pétrole, 65(3), 445-459. https://doi.org/10.2516/ogst/2009028
- Bossie-Codreanu, D. (2017). Study of N2 as a mean to improve CO2 storage safety. *Energy Procedia*, 114, 5479-5499. https://doi.org/10.1016/j.egypro.2017.03.1691
- Brun, K., & Allison, T. (2022). Machinery and Energy Systems for the Hydrogen Economy. Elsevier.
- Busch, A., Alles, S., Gensterblum, Y., Prinz, D., Dewhurst, D. N., Raven, M. D., & Stanjek, H. K. (2008). Carbon dioxide storage potential of shales. *International journal of greenhouse gas control*, 2(3), 297-308. https://doi.org/10.1016/j.ijggc.2008.03.003
- Busch, A., Bertier, P., Gensterblum, Y., Rother, G., S. C., Zhang, M., & Wentinck, H. M. (2016).
 On sorption and swelling of CO2 in clays. *Geomechanics and Geophysics for Geo-energy* and Geo-resources, 2, 111-130. https://doi.org/10.1007/s40948-016-0024-4
- Busch, A., Kampman, N., Hangx, S. J., Snippe, J., Bickle, M., Bertier, P., & Schaller, M. (2014).
 The Green River natural analogue as a field laboratory to study the long-term fate of CO2 in the subsurface. *Energy Procedia*, 63, 2821-2830. https://doi.org/10.1016/j.egypro.2014.11.304
- Carneiro, J. F., Matos, C. R., & Van Gessel, S. (2019). Opportunities for large-scale energy storage in geological formations in mainland Portugal. *Renewable and Sustainable Energy Reviews*, 99, 201-211. https://doi.org/10.1016/j.rser.2018.09.036

Carriveau, R., & Ting, D. S. (2016). Methane and hydrogen for energy storage (No. 137811). IET.

- Cerasi, P., Duda, M., Edvardsen, L., Agofack, N., & Bhuiyan, M. H. (2022). Effect of Field Caprock Shale Exposure to CO2 on Its Mechanical Properties—A Comparison of Experimental Techniques. *Physical Sciences Forum*, 4(1), 33. https://doi.org/10.3390/psf2022004033
- Eshiet, K., & Sheng, Y. (2014). Investigation of geomechanical responses of reservoirs induced by carbon dioxide storage. *Environmental Earth Sciences*, *71*, 3999-4020. https://doi.org/doi.org/10.1007/s12665-013-2784-2

- Fjaer, E., Holt, R. M., Horsrud, P., & Raaen, A. M. (2008). *Petroleum related rock mechanics*. Elsevier.
- Gluyas, J., & Mathias, S. (2013). Geological storage of carbon dioxide (CO2): geoscience, technologies, environmental aspects and legal frameworks. Elsevier.
- Hangx, S., Bakker, E., Bertier, P., Nover, G., & Busch, A. (2015). Chemical–mechanical coupling observed for depleted oil reservoirs subjected to long-term CO2-exposure–A case study of the Werkendam natural CO2 analogue field. *Earth and Planetary Science Letters*, 428, 230-242. https://doi.org/10.1016/j.epsl.2015.07.044
- Hassannayebi, N., Azizmohammadi, S., De Lucia, M., & Ott, H. (2019). Underground hydrogen storage: application of geochemical modelling in a case study in the Molasse Basin, Upper Austria. *Environmental Earth Sciences*, 78, 1-14. https://doi.org/10.1007/s12665-019-8184-5
- Ilgen, A. G., Newell, P., Hueckel, T., Espinoza, D. N., & Hu, M. (2019). Coupled chemicalmechanical processes associated with the injection of CO2 into subsurface. *Science of carbon storage in deep saline formations*, pp. 337-359. https://doi.org/10.1016/B978-0-12-812752-0.00015-0
- Lamy-Chappuis, B., Angus, D., Fisher, Q. J., & Yardley, B. W. (2016). The effect of CO2-enriched brine injection on the mechanical properties of calcite-bearing sandstone. *International Journal of Greenhouse Gas Control*, 52, 84-95. https://doi.org/10.1016/j.ijggc.2016.06.018
- Li, Z., Su, Y., Shen, F., Huang, L., Ren, S., Hao, Y., Wang, W., Meng, Y., & Fan, Y. (2023).
 Investigation of CO2 storage and EOR of alternating N2 and CO2 injection using experiments and numerical simulation. *Fuel*, 340. https://doi.org/10.1016/j.fuel.2023.127517
- Loret, B., Hueckel, T., & Gajo, A. (2002). *International Journal of Solids and Structures, 39*(10), 2773-2806. https://doi.org/10.1016/S0020-7683(02)00151-8
- Matos, C. R., Carneiro, J. F., & Silva, P. P. (2019). Overview of large-scale underground energy storage technologies for integration of renewable energies and criteria for reservoir identification. *Journal of Energy Storage*, 21, 241-258. https://doi.org/10.1016/j.est.2018.11.023
- Ojala, I. O. (2011). The effect of CO2 on the mechanical properties of reservoir and cap rock. *Energy Procedia*, 4, 5392-5397. https://doi.org/10.1016/j.egypro.2011.02.523

- Peter, A., Yang, D., Eshiet, K. I., & Sheng, Y. (2022). A Review of the Studies on CO2–Brine– Rock Interaction in Geological Storage Process. *Geosciences*, 12(4), 168. https://doi.org/10.3390/geosciences12040168
- Rohmer, J., Pluymakers, A., & Renard, F. (2016). Mechano-chemical interactions in sedimentary rocks in the context of CO2 storage: Weak acid, weak effects? *Earth-Science Reviews*, 157, 86-110. https://doi.org/10.1016/j.earscirev.2016.03.009
- Rother, G., Ilton, E. S., Wallacher, D., Hauβ, T., Schaef, H. T., Qafoku, O., Rosso, K. M., Felmy,
 A. R., Krukowski, E. G., Stack, A. G., N., G., & Bodnar, R. J. (2013). CO2 sorption to subsingle hydration layer montmorillonite clay studied by excess sorption and neutron diffraction measurements. *Environmental science & technology*, 47(1), 205-211. https://doi.org/10.1021/es301382y
- Rutqvist, J. (2012). The geomechanics of CO2 storage in deep sedimentary formations. Geotechnical and Geological Engineering, 30(525-551). https://doi.org/10.1007/s10706-011-9491-0
- Rutqvist, J., Vasco, D. W., & Myer, L. (2010). Coupled reservoir-geomechanical analysis of CO2 injection and ground deformations at In Salah, Algeria. *International Journal of Greenhouse Gas Control, 4*(2), 225-230. https://doi.org/10.1016/j.ijggc.2009.10.017
- Sun, Y., Aman, M., & & Espinoza, D. N. (2016). Assessment of mechanical rock alteration caused by CO2 - water mixtures using indentation and scratch experiments. *International Journal* of Greenhouse Gas Control, 45, 9-17. https://doi.org/10.1016/j.ijggc.2015.11.021
- Tarkowski, R., Uliasz-Misiak, B., & Tarkowski, P. (2021). Storage of hydrogen, natural gas, and carbon dioxide–Geological and legal conditions. *International Journal of Hydrogen Energy*, 46(38). https://doi.org/10.1016/j.ijhydene.2021.03.131
- Tian, H., Pan, F., Xu, T., McPherson, B., Yue, G., & Mandalaparty, P. (2014). Impacts of hydrological heterogeneities on caprock mineral alteration and containment of CO2 in geological storage sites. *International Journal of Greenhouse Gas Control, 24*, 30-42. https://doi.org/10.1016/j.ijggc.2014.02.018
- Zhou, J., Deng, G., Tian, S., Xian, X., Yang, K., Zhang, C., & Dong, Z. (2023). Experimental study on the permeability variation of sandstone at cyclic stress: Implication for underground gas storage. *Journal of Energy Storage*, 60. https://doi.org/10.1016/j.est.2023.106677