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Thermal Shock Sensitivity of Limestone Rock Under Rapid CO_2-Induced Cooling

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Abstract

Carbon dioxide (CO_2) is a major contributor of global warming. Reducing CO_2 emissions remain a major challenge, with several emerging solutions. Carbon capture and storage (CCS) is a viable option for reducing CO_2, either extracted directly from the atmosphere or captured from industrial processes. In CCS, CO_2 is collected from major emission sources and stored securely in deep geological formations such as depleted oil fields, deep coal seams, and saline aquifers. During the injection of CO_2, a transition from gas to liquid phase occurs, which is associated with rapid cooling. This sudden cooling results in internal stress in the rock environment. This process can fracture host rocks, produce induced seismicity and reduce the safety and security of storage sites. This study investigated the impact of cyclic thermal shock on the mechanical properties of limestone rock through laboratory testing. A total 24 limestone specimens were subjected to thermal treatment of up to 12 thermal shocks. Each cycle involved heating the sample for 2 hours in an oven 55°C and then placing this heated sample in a freezer at -17°C for 2 hours to simulate thermal shock associated with CO_2 injection. UCS and BTS tests were conducted at 0, 3, 6, 9, and 12 cycles, along with ultrasonic pulse velocity (UPV) measurements to monitor internal structural changes. The results showed a consistent decrease in tensile strength, with 42% decrease for 12 cycles of thermal shock. Whereas, compressive strength showed a slight decrease, indicating that the tensile strength of limestone is more sensitive to thermal shock cycles than compressive strength. Interestingly, UPV increased despite strength degradation, likely due to micro-pore closure and grain-contact rearrangement. Overall, the results showed that cyclic thermal shocks can weaken the limestone, specifically in tension, and should be considered while designing and monitoring of CO_2 storage in limestone reservoirs.

Keywords

Carbon Capture and Storage (CCS), Limestone, Rapid cooling, Heating.

1 Introduction

Global warming is one of the biggest challenges of the 21st century, and Carbon dioxide (CO_2) is the dominant driver behind it. The CO_2 emissions are a threat to human life and have resulted in the rise of global temperature, an increase in sea level, adverse climate conditions, and many natural disasters such as floods and droughts (Cheng et al., 2024). To mitigate this problem, it is essential to decarbonize the environment and store the CO_2 in long-term safe storage. Considerable research has been done to develop technologies for CO_2 storage. Among these, carbon capture and storage (CCS) is one of the most promising solutions and a practical solution for reducing CO_2 without affecting the industrial productivity (Celia, 2017).

Geological Storage of CO_2 (GSC) is one of the important parts of CCS in which CO_2 captured from major emission sources or the environment is stored securely in deep geological formations such as depleted oil fields, deep coal seams, and deep saline aquifers (Eyitayo et al., 2025). The process mimics the natural trapping mechanism through which oil and gas remain safely stored in underground rock formations for millions of years. Compressed CO_2 under high pressure is injected into the geological formations through injection wells. This process can lead to rapid cooling (Joule Thomson effect) of reservoir rock around the injection well due to expansion of injected CO_2 as it enters from high pressure system to low pressure reservoir (Mok et al., 2026). This rapid cooling causes the development of internal stresses in the rock and significantly affects the mechanical properties of the rock. Therefore, it is essential to investigate the mechanical behaviour of rock corresponding to this cooling.

Previous studies on the thermal response of cap rock and reservoir rock during CO_2 injection mostly relied on numerical modelling, with very few experimental studies. Vilarrasa et al. (2014) studied the effect of cold CO_2 injection on cap rock and reservoir stability over long-term operation using thermo-hydro-mechanical simulations. It was observed that cold CO_2 injection induces thermal stress changes that reduce the reservoir stability; on the other hand, it enhances cap rock stability. Similarly, this numerical study also demonstrated that although thermal stresses from cold CO_2 injection reduces the reservoir stability but enhances the cap rock integrity, and these stresses are unlikely to cause fracture propagation or leakage (Vilarrasa & Laloui, 2015). Using an elastoplastic thermomechanical model, this study simulated the cold CO_2 injection in deep saline aquifers and investigated under what conditions thermal stresses can jeopardize the cap rock integrity. Their results showed that cold injection induces inelasticity in the reservoir, but fractures do not propagate into the cap rock. Moreover, some localized yielding can occur in the lower portion of the cap rock; however, this damage is limited and does not compromise the cap rock's sealing ability (Vilarrasa & Laloui, 2016). In another study, numerical modelling was used to simulate how the temperature difference between the injected CO_2 and the reservoir influences the fracture propagation and damage. The study concluded that fracture growth during CO_2 is dependent on temperature and in-situ horizontal effective stress (Roy et al., 2018). Similarly this study used a thermoelastic 3D model to simulate cold CO_2 injection and its effect on fracture aperture growth in a field-scale reservoir. The findings of the study highlighted that contraction increases the fracture apertures within the reservoir but reduces them in the cap rock. The fracture behaviour is strongly dependent stress condition, orientation and proximity to the injection well. Overall thermal effects significantly influence fracture dynamics and integrity of the reservoir (Salimzadeh et al., 2018). In contrast to previous researches this experimental study evaluated the effect of rapid quenching on the core samples from Salah CO_2 storage site, Krechba field, Algeria. The samples were heated up to various temperatures (50, 150, 250, 350 and 500°C) and then rapidly quenched to room temperature 20°C. Permeability, along with P&S wave were measured before and after the thermal treatment. The study concluded that the effect of thermal shock at the Krechba field is negligible as the expected cooling (~65°C) caused insignificant changes in permeability and seismic velocities (Blake et al., 2022).

In this study, we aim to determine the effect of cyclic thermal shock on the mechanical properties of limestone reservoir rock through controlled laboratory experiments. The rock samples were heated up to 55°C and then rapidly cooled to -20°C to simulate the thermal conditions associated with cold CO_2 injection. The results of this study are expected to provide more comprehensive understanding of how repeated thermal shocks influence the stability and durability of limestone rock and help in the design and maintenance of the carbon storage sites in the long term.

2 Materials and Methods

A total of 30 limestone samples were used in this study. The limestone belongs to the Miocene porous limestone formation of the Budapest region (Hungary). Its micro-fabric is primarily an ooidal grainstone packstone. A total of 15 UCS and 15 BTS samples were prepared; 3 samples from each category were tested before the thermal shock cycles, whereas the remaining 24 samples are illustrated in Figure 1. Prior to thermal treatment, all samples were oven dried at 100°C for 24 hours to remove moisture. After drying the samples were cooled at room temperature before the start of cyclic thermal treatment.



Fig. 1 Porous limestone samples.

Cyclic thermal shock was applied to simulate the rapid cooling around the injection well bore outlet during CO_2 injection in geological formations. Each cycle consisted of two phases: heating and cooling. During the heating phase the samples were placed in an oven with 55°C temperature for 2 hours. After 2 hours, the heated samples were directly transferred to a freezer at -17°C temperature and the samples were cooled for 2 hours to simulate rapid cooling and induce stresses in the rock samples. After cooling, the samples were placed at room temperature for stabilization, and this sequence constituted one cycle. The heating temperature of 55°C was estimated for a representative of GCS site of 1500m depth by applying a typical geothermal gradient 30°C/ Km to a baseline surface temperature of 10°C. Moreover, the cooling temperature of -17°C was used due to laboratory constraints as the refrigerator in the laboratory could achieve only up to -17°C temperature. The duration of 2 hr was selected to ensure a uniform temperature distribution throughout the rock specimens.

The mechanical testing was done on five predefined stages corresponding to 0 (untreated), 3, 6, 9 and 12 thermal cycles. At each stage the ultrasonic pulse velocity along with weight was recorded for each sample. Moreover, at each stage three samples were tested for UCS and other 3 for BTS. The average of three samples was taken as representative strength for each phase. This phased approach was adopted to evaluate the progressive changes in the mechanical properties with increase in thermal shock cycles exposure. Uniaxial compressive strength tests were performed on the cylindrical specimens using a compression testing machine under controlled loading conditions. Load was applied axially at a constant rate until specimen failure, and the peak stress was recorded as the UCS. Brazilian tensile strength tests were conducted by applying diametrical compression to the disc specimens until failure occurred. The tensile strength was calculated from the peak load using standard formulations for the Brazilian test. The experimental results obtained from UCS and BTS were analysed to assess the influence of thermal cycles on the mechanical properties of limestone reservoirs. Variation in strength values across thermal cycles was evaluated to identify the trend of degradation.

3 Results and Discussion

3.1 Brazilian Tensile Strength

The variation of Brazilian tensile strength with thermal shock cycles is presented in Figure 2.The results clearly show a decreasing trend of tensile strength with an increase in thermal shock cycles. The untreated samples (0 cycles) exhibited the highest average strength, approximately 0.96 `. After 3 cycles average strength reduced to 0.88 MPa, which further declined to 0.79 MPa at cycles. A slight

increase in tensile strength is observed at 9 cycles (0.82 MPa). This deviation does not change the overall trend and can be attributed to natural heterogeneity in the limestone rock. After 12 cycles, the strength significantly dropped to 0.56 MPa, representing an overall reduction of 42% tensile strength.

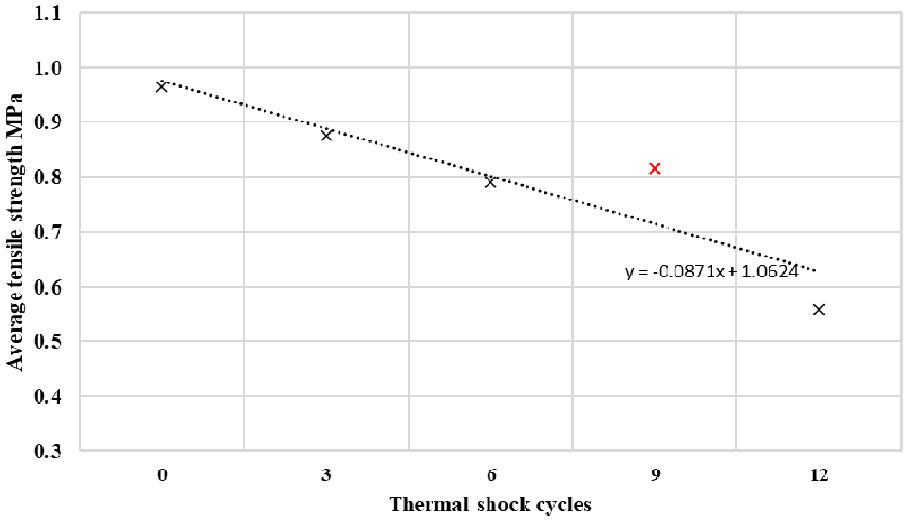


Fig. 2 Variation of tensile strength with thermal shock cycles.

3.2 Unconfined Compression Strength

The variation of compressive strength with thermal cycles is shown in Figure 4. The results overall show a decrease in UCS strength with an increase in thermal shock cycles. The untreated samples exhibited the highest strength of 5.24 MPa, which decreased slightly after the first three cycles to 5.17 MPa. Similarly, the strength again decreased to 4.86 MPa after 6th cycle. However, on 9th cycle significant decrease in strength to 2.99 MPa was observed, and after the 12th cycle, the strength was regained up to 4.25 MPa. The large reduction in strength at the 9th cycle was abnormal to the trend, and possible reason could be some pre-existing defects or cracks in the samples. Overall, the trend shows a gentle decrease in the UCS strength with an increase in thermal shock cycles.

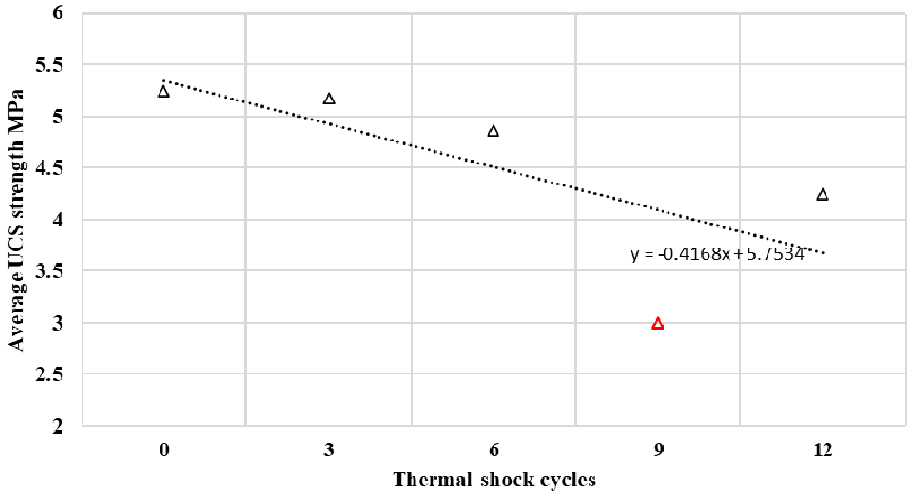


Fig. 3 Variation of UCS strength with thermal shock cycles.

The variation of ultrasonic pulse velocity (UPV) with thermal cycles is presented in Figure 3. The results show a general increase in velocity with an increase in the number of thermal cycles. This trend appears inconsistent to the degradation of strength in BTS and UCS. The possible explanation for it could be that repeated heating and cooling can cause partial closure or rearrangement of micro-pores and grain contacts, improving wave transmission locally even though the overall mechanical strength decreases. Further detailed investigation is required to evaluate this anomaly.

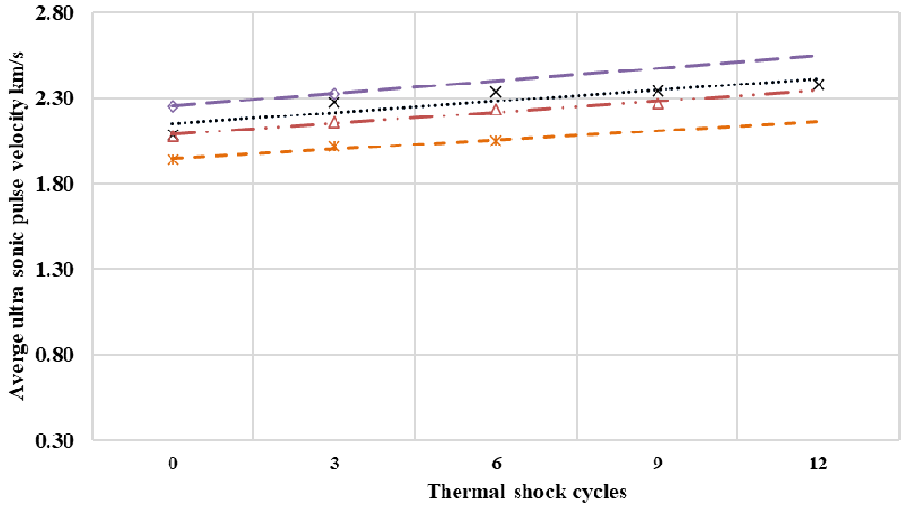


Fig. 4 Variation of ultrasonic pulse velocity with thermal shock cycles.

The failure plane angles after the UCS test showed major variations (Figure 5). It is clearly visible from the Figure that the failure plane progressively shifted towards steeper orientations. Particularly at higher cycles 9 and 12 cycles the failure plane appeared more vertical, indicating a transition towards axial splitting and tensile dominant failure. This change in failure mechanism suggests that cyclic thermal shock cycles induce micro cracks in limestone and reduce its cohesion.

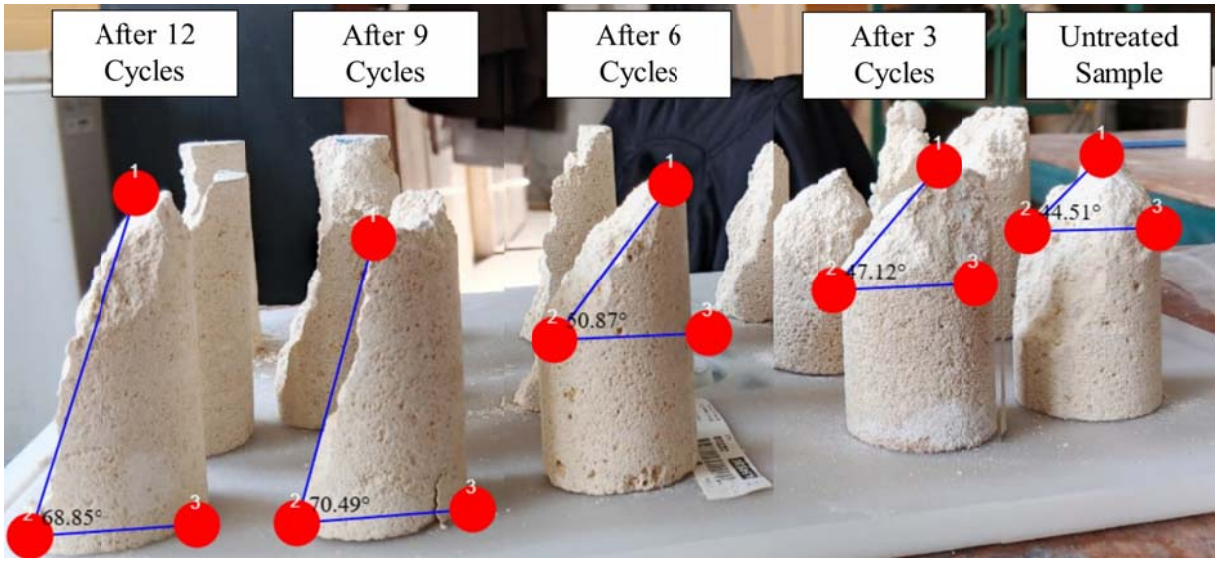


Fig. 5 Fracture patterns and corresponding failure angles observed in limestone specimens after rapid CO_2 cooling.

While the experimental result provides useful insightful into the thermal shock sensitivity of limestone rock. However, it is important to highlight that experiments in this study were conducted in laboratory do not completely represent the in situ thermo-mechanical environment of deep geological storage site. Future studies should investigate the thermomechanical behaviour under in situ stress conditions and field representative temperatures to simulate actual reservoir conditions.

4 Conclusions

This study investigated the effect of thermal cyclic shock associated with CO_2 injection on the mechanical behaviour of limestone rock. Based on experimental results of UCS and BTS along with UPV following conclusions can be drawn:

I. The tensile strength of limestone degrades progressively with the increase in thermal cycles. 42% reduction in tensile strength was observed after 12cycles of thermal shocks. This indicates that even moderate cyclic thermal shocks can weaken the limestone in tension

II. UCS strength also showed a declining trend with an increase in thermal cycles; however, degradation was very less compared to tensile strength. Overall, the compressive strength of limestone is less sensitive to thermal shock cycles.

III. UPV increased slightly with an increase of thermal shock cycles, which is inconsistent with the degradation of UCS and BTS and requires further investigation.
IV. Visual observation of failed UCS specimen indicate that the failure plane shifts from inclined to vertical, showing that the failure mechanism changes from shear to tensile failure with an increase in thermal shock cycles.

Overall, this study highlights that even cyclic thermal shock with moderate temperature can significantly affect the mechanical behaviour of limestones. Therefore, thermal shock effects should be considered in the design and monitoring of CO_2 storage in limestone reservoirs.

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