Effect of cyclic thermal loading on a carbonate rock: implications for thermal energy storage

Katharina Meta Neumann
Engineering Geology and Rock Mass Mechanics, Ruhr-Universität Bochum, Germany

Mandy Duda
Engineering Geology and Rock Mass Mechanics, Ruhr-Universität Bochum, Germany

Tobias Backers
Engineering Geology and Rock Mass Mechanics, Ruhr-Universität Bochum, Germany

ABSTRACT: Because renewable energy, such as wind and solar energy, is subject to temporal fluctuations, solutions are needed to store the energy in order to use it during periods of low energy production. Sensible thermal energy storage in rock (e.g. Alami et al. 2020) and seasonal geothermal energy storage are two options among some. The cyclic heating and cooling of the rock associated with cyclic storage can cause variations in the rock's thermo-hydromechanical properties (Fränzer et al. 2023). To understand and specify those changes different rocks from a Jurassic carbonate rock formation in Southern Germany, a formation also targeted for geothermal use, was characterised before and after cyclic thermal loading. We investigated elastic, inelastic and thermal properties before and after thermal treatment to 100 °C and 800 °C. The results contribute to the understanding of thermally-induced changes in properties of rock and rock mass relevant for thermal energy storage.

Keywords: thermal cycling, sensible heat thermal energy storage, limestone, carbonate rocks, thermal and mechanical properties.

1 INTRODUCTION

Thermal energy storage has become increasingly relevant in the context of challenges arising from climate change and sustainable energy provision. The availability of wind and solar energy, for example, varies with time. Also, geothermal energy systems at intermediate depths may serve as seasonal thermal energy storage when surplus energy is available.

Besides latent and thermo-chemical heat storage, sensible heat storage has been used since long (Esence et al. 2017). Low- to intermediate-depth geothermal reservoirs are considered as vital thermal storage systems, but also packed-bed storage units above ground. Rock is a popular material for sensible heat storage because of its abundance, availability and thermal stability in a wide temperature range (Tiskatine et al. 2017). Here, we investigate the suitability of carbonate rocks as potential thermal energy storage medium, also, because many geothermal systems are successfully used for thermal energy provision in carbonate rock mass.

Carbonate rocks have been subject to previous investigations in the context of thermal energy storage. Tiskatine et al. (2016) treated 13 rock samples from Morocco to 650 °C. The four limestones

used in this study had a calcite content of 95 %. The limestones formed a white dust layer of varying thickness after 12, 24, 70 and 90 heating cycles, respectively. Three limestones fractured. It was concluded that quartz and calcite control the rocks physico-mechanical properties. Additionally, it is described that the cracking of the limestone is due to a loss of mass introduced by CO_2 emission during decomposition of $CaCO_3$. The cracking increases during thermal cycling causing an increase in open porosity and a decrease in hardness. Results of Becattini et al. (2017) were in agreement with Tiskatine et al. (2016). They treated six alpine rock to 110 – 600 °C. They found that the specific heat capacity decreases and the porosity increases after cyclic thermal treatment, which is explained by physical and chemical reactions such as mineral dehydration, quartz-inversion reaction and decarbonation. It is concluded that limestone is unsuitable for thermal-energy storage at temperatures above 600 °C due to its high calcite content and fracturing of the rock during thermal treatment. Villarraga et al. (2018) pursued a different approach with lower temperatures and more than 1000 cycles. A temperature range of 10 – 50 °C was applied corresponding to the range of climatic actions and the evaluation of the results regarding rockfall problematics. The selected karstified limestone from the Coniancian (Late Cretaceous) in France showed an accumulation of deformation, decrease in uniaxial compressive strength, P- and S-wave velocity, but no noticeable change in porosity.

Because geothermal storage systems operate at temperatures between roughly 60 °C to > 100 °C, and thermal packed-bed energy storage can exhibit temperatures of 750 °C and beyond (e.g. Siemens Gamesa.com), we selected two heating temperatures that reflect both applications, i.e., we heated our samples to 100 °C or 800 °C. We specifically addressed the following questions: 1) How does heating to the two temperatures affect properties of carbonate rocks relevant to thermal energy storage? 2) Can carbonate rocks be considered a suitable medium for thermal energy storage?

2 MATERIAL AND METHODS

The rock samples were chosen from two different quarries in the Franconian Alb (Southern Germany). Saal a. d. Donau is located along the Danube in the Southern Franconian Alb, while Sengenthal is in the central Franconian Alb between the cities of Nuremberg and Regensburg. The selected rocks are from the Oxfordian (6, 7 and 8 from Segenthal) and from the Lower Thithonian to Kimmeridgian (9, 15 and 17 from Saal a. d. Donau). All rocks represent limestones and differ in color, grain size, mineralogy, porosity, and fossil content.

The mineralogical composition of each rock sample was determined with X-ray powder diffraction analysis (XRPD). The results in terms of weight-% were evaluated by applying the Rietveld method. For uniaxial compressive strength tests, thermal properties and basic physical characterization cores with a diameter of about 40 mm or 30 mm were diamond-drilled and sawed and ground square within 0.02 mm parallelism to a length of about 80 mm (diameter of 40 mm) or 60 mm (diameter of 30 mm). Additional samples were prepared and sawed to a length of about 20 mm (diameter of 40 mm) or 15 mm (diameter of 30 mm) for splitting tensile strength tests. Throughout the preparation water was used as cooling fluid.

Bulk densities were determined through the ratio of mass to bulk volume of the oven-dried samples. Total porosities were calculated from the ratio of bulk density of drilled samples to grain density (from pycnometry). Ultrasound P- and S-wave velocities were determined with a standard measurement device (Geotron Elektronik) with S-wave sensors for the cylindrical samples used for uniaxial compressive strength tests. Two identical ultrasound sensors were pneumatically loaded to the end faces of the samples in axial or radial direction. Solid elastic silicon with a thickness of about 1 mm was used as a coupling medium. The waveform generator generates a rectangular source with a frequency of about 350 kHz. Signals were semi-automatically analysed using the software LightHouse UMPC (Rentsch & Krompholz 1961).

Thermal conductivities were determined using C-Therm's Trident system with the Modified Transient Plane Source (MTPS) on cylindrical samples (Harris et al. 2014). The semi-automatic measurement technique applies a current to the sensor's spiral heating element that provides a small amount of heat causing a temperature signal of 1 to 3 °C, which is one-dimensionally transferred into the measured end face of the sample (ASTM D7984-16 2016). Distilled water was used as a coupling agent and a 500 g weight on top of the sample was used to further improve and standardize coupling.

Uniaxial compressive strength tests were performed with a stiff 4000 kN loading frame. The cylindrical samples were centered between the loading plates. A radial strain chain was placed around the center of the sample. The axial piston advanced with a constant velocity resulting in a strain-rate of about 10^{-5} mm/mm/s. Axial stresses and strains were calculated with the cross-sectional area of the sample before testing and maximum sample length. The axial strain was calibrated for the deformation of the assembly. Uniaxial compressive strength σ_c was derived from the maximum in the stress-strain-relation.

For splitting tensile strength tests cylindrical sample discs were placed in the center of a steel loading jaw. An initial load of 100 to 200 N was applied. Further strain was applied with a rate of 2,5 µm/s until failure occurred (ISRM 1978). Tensile stress was calculated using the following equation:

$$\sigma_t = \frac{2}{\pi} \cdot \frac{F}{D \cdot L}$$

The splitting tensile strength $\sigma_{t,sp}$ was determined from the maximum of tensile stress in the conducted splitting tensile strength tests.

Samples of the six rock types were cyclically heated with a rate of 1,56 K/min to either 100 °C or 800 °C in three cycles. The temperature was kept constant for 0,5 h, then cooled to 30 °C and held for another 0,5 h, before the next cycle started. While basic physical, dynamic elastic and thermal properties were measured for the same samples before and after heat treatment (see subsample specification in figures), uniaxial compression and splitting tensile strength tests were performed on individual samples.

3 RESULTS

All investigated samples are mainly composed of calcite (97 – 100 %; Table 1). Minor constituents are represented by quartz (up to 1 %) and clay minerals (up to 2 %). No signs of dolomitization were evident from XRD analysis.

Table 1. Results of XRD analysis for samples 6, 7, 8, 9, 15 and 17 in weight-%. The error depends on the mineral fraction and is about +/- 2.5 %.

Sample		6	7	8	9	15	17
Calcite	[%]	97.0	98.0	98.0	100.0	100.0	98.5
Quartz	[%]	1.0	1.0	1.0	traces?	traces?	1.0
Clay minerals	[%]	2.0	1.0	1.0	traces?	traces?	0.5

Bulk densities of samples were not significantly affected by heating to 100 °C. Densities were consistently slightly higher after heating to 100 °C but did not exceed experimental uncertainties. Heating to 800 °C significantly decreased bulk densities. Samples were visibly damaged with thermal cracks causing the outer layer of the samples to chip off easily.

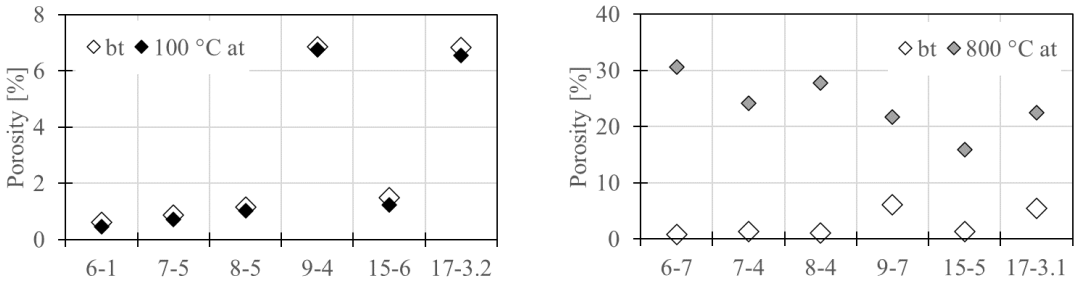

Figure 1. Total porosities of untreated (bt) and thermally treated samples (100 °C at, 800 °C at).

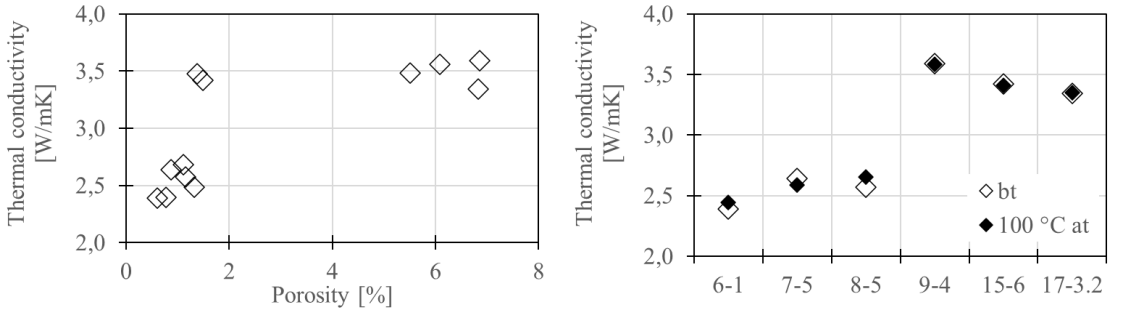

Figure 2. Left: Thermal conductivities of untreated samples vs. porosity. Right: Thermal conductivities of untreated (bt) and thermally treated samples (100 °C). No data was obtained for samples heated to 800 °C.

Samples exhibited low to medium total porosities prior to thermal treatment (Figure 1). Total porosities of untreated samples ranged from 0.6 % to 6.9 %. Elevated total porosities were determined for samples 9 and 17 from Sengenthal. From that quarry, sample 15 shows total porosities as low as those determined for samples 6 to 8 (< 2 %). The effect of thermal treatment on bulk densities is reflected in terms of total porosities: After heating to 100 °C total porosities remained nearly constant with a tendency to a slight decrease in porosity, while porosities were significantly higher after heating to 800 °C.

Thermal conductivities were not affected by heating to 100 °C and ranged from 2,4 to 3,6 W/m.K (Figure 2). Counterintuitively, thermal conductivities roughly scale with total porosity, i.e., thermal conductivity is larger for samples with higher porosities, except for sample 15-6, which shows a high thermal conductivity while also being low in porosity.

Ultrasound P-wave velocities in axial direction ranged from 4318 to 5919 m/s prior to thermal treatment (Figure 3). Axial S-wave velocities ranged from 2773 to 4019 m/s with an average P-to-S-ratio of 1,6. Radial velocities did not differ systematically from those measured in axial direction, but individual samples show differences beyond measurement uncertainty pointing to some anisotropy. The difference between axial and radial velocities was larger for S-wave velocities before thermal treatment than for P-wave velocities. Heating to 100 °C did not affect P- and S-wave velocities (Figure 3). Heating to 800 °C reduced P- and S-wave velocities significantly in axial and radial direction. The difference between thermal responses in axial and radial direction indicate that heating resulted in anisotropic thermal damage. The amount of velocity reduction differed significantly among individual samples.

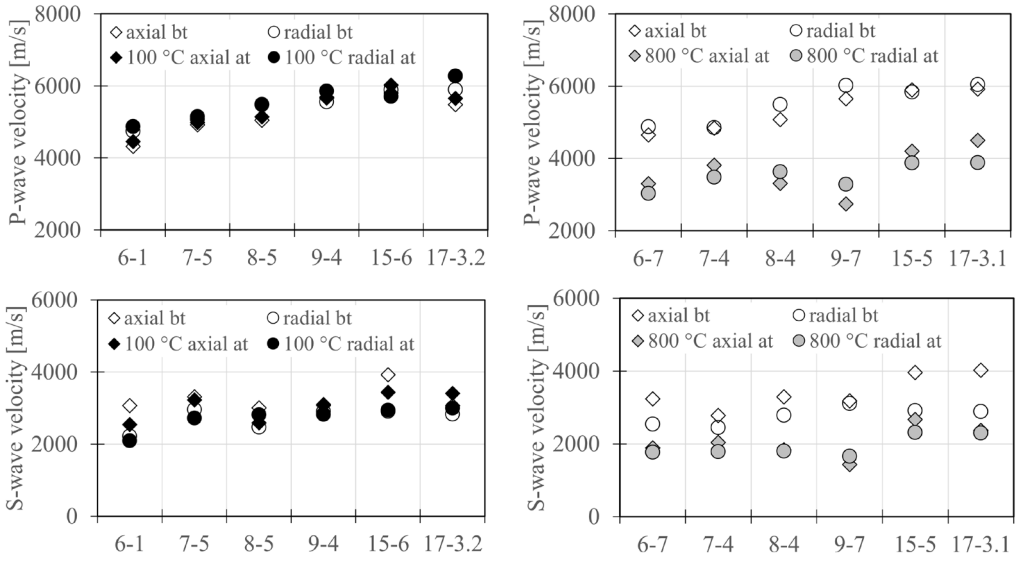

Figure 3. P-wave velocities (top) and S-wave velocities (bottom) in axial (diamonds) and radial (circles) direction for untreated samples (bt) and thermally treated samples (100 °C/800 °C axial/radial at).

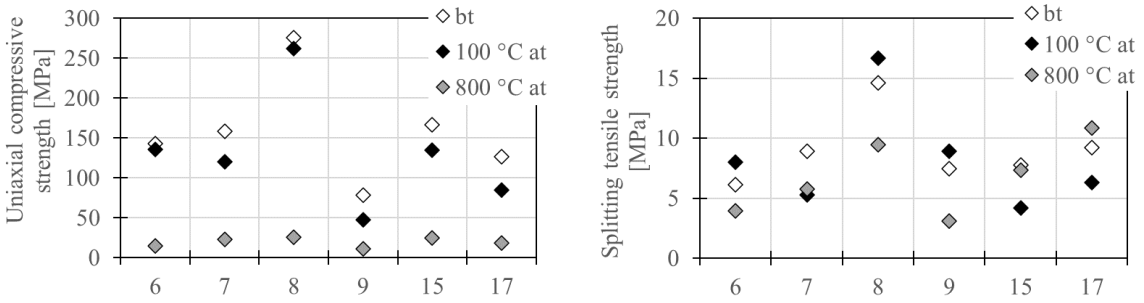

Figure 4. Uniaxial compressive strength (left) and splitting tensile strength (right) for untreated (bt) and thermally treated samples (100 °C at, 800 °C at).

4 DISCUSSION

Based on the results obtained for the investigated samples, thermal heating alters the mechanical properties of carbonate rocks. Heating to as low as 100 °C reduced the uniaxial compressive strength of the rock. Ultrasound velocities, porosity and thermal conductivity did not change upon heating to 100 °C.

We did not investigate the effect of the number of thermal cycles. Fränzer et al. (2023) reported a systematic effect on several properties for a heating temperature of 800 °C for up to 15 cycles. A comprehensive analysis of anisotropic transport properties including hydraulic properties is ongoing and will help to better understand the implications for seasonal thermal energy storage in carbonate geothermal systems.

Heating to 800 °C strongly affected elastic and inelastic properties of the investigated carbonate rock samples. Their uniaxial strength reduced to less than 20 % of its initial value. Porosities increased and ultrasound velocities decreased both in radial and axial direction. No thermal properties could be determined. We assume that coupling to the mechanically disintegrated outer sample layer and exothermal reactions with the coupling agent might have caused the lack of a thermal response. Samples heated to 800 °C showed signs of decarbonation, i.e. the chemical decomposition of $CaCO_3$ to CaO and CO_2, which is indicated by a white, powdery layer at the sample's surface (CaO; Tiskatine et al., 2016). Decarbonation has been reported to occur at temperatures above 800 °C, but starts at lower temperatures and is probably the cause for the degradation of mechanical properties.

The changes in mechanical properties of the investigated carbonate rock samples, the powdered structure of fragments after mechanical disintegration potentially clogging fluid pathways (Becattini et al, 2017) indicate that carbonate rocks are less suitable for use in high temperature packed-bed thermal energy storage. We will, however, continue to further investigate the thermomechanical response to cyclic loading, because the low thermal conductivity of CaO may also contribute to better thermal storage properties than siliciclastic rocks at high temperatures (e.g. Aihara et al., 2001).

5 CONCLUSION

We investigated the thermomechanical response of six different carbonate rocks to thermal heating to 100 °C and 800 °C. We found that heating to 100 °C reduced uniaxial compressive strength, but ultrasound velocity, total porosity, thermal conductivity and, apparently, tensile strength remained unaffected or within sample-to-sample variability. Heating to 800 °C significantly altered the investigated properties, in particular uniaxial compressive strength, which was reduced to less than 20 %, but also porosity and ultrasound velocities.

Based on the results from this study, the properties relevant to thermal energy storage of the investigated carbonate rocks seem to be rather resistant to heating at lower temperatures, but more specific investigations regarding the effect of number of cycles and the impact of microstructural properties are required. Due to decarbonation, the properties of carbonate rocks are very sensitive to

heating at higher temperatures. Although an application as packed-bed thermal energy storage medium does not seem practical, the potentials of decarbonation during thermal storage in rocks may deserve more attention.

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