



# Experimental investigation of the thermal and mechanical stability of rocks for high-temperature thermal-energy storage



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## HIGHLIGHTS

- Six Alpine rocks were investigated for high-temperature thermal-energy storage.
- The rocks were cycled between 100 and 600 °C with a heating rate of 2.6 °C/min.
- Cycling decreases the specific heat capacity and increases the porosity.
- The changes induced by cycling are attributed to physical and chemical reactions.
- Rocks suitable for high-temperature thermal-energy storage were identified.

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## ABSTRACT

Six types of rocks of Alpine origin were investigated for their suitability for high-temperature packed-bed thermal-energy storage. The rocks were thermally cycled in laboratory furnaces between about 100 °C and 600 °C with a heating rate of 2.6 °C/min and assessed in terms of their specific heat capacity and porosity as well as the degree of cracking, fracturing, and disintegration. Thermal cycling was found to lead to decreases in the specific heat capacity and increases in the porosity of the rocks. These changes are explained by physical and chemical reactions such as mineral dehydration, deserpentinization, decarbonation, and the quartz-inversion reaction. Simulations of a 23 MWh industrial-scale thermal-energy storage show that the decrease in the specific heat capacity does not have a significant impact on the effective storage capacity, utilization factor, and exergy efficiency. To avoid fracturing of rocks, foliated rocks and rocks rich in calcite and/or quartz, such as limestones and sandstones, are found to be unsuitable when exposed to temperatures higher than about 600 °C or 573 °C, respectively. Mafic rocks, felsic rocks, serpentinite, and quartz-rich conglomerates are judged to be suitable for high-temperature thermal-energy storage.

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## 1. Introduction

Meeting the rising global energy demand and mitigating the effects of climate change require the exploitation of renewable energy sources. Because most of these sources are intermittent, making them available around-the-clock requires energy storage. Thermal-energy storage (TES) is a storage technology that is already used in concentrated solar power (CSP) plants, see Kuravi et al. [1], and will be a key component of advanced adiabatic compressed air energy storage (AA-CAES) power plants, see Budt et al. [2].

TES systems that store thermal energy in the form of sensible heat are the simplest, most mature, and hence most widely used. For CSP plants that use thermal oils or molten salts as the heat-transfer fluid (HTF), a common sensible TES system is two-tank molten-salt storage, see Kearney et al. [3] and Herrmann et al. [4]. This system has several disadvantages. First, the relatively high solidification temperatures of molten salt (about 220 °C for solar salt) necessitate the installation of heaters. Second, the relatively low maximum temperatures of molten salt (about 600 °C for solar salt) limit power-block efficiencies. Third, the comparatively high costs of molten salt and the need for two tanks result in high storage-system costs. These disadvantages can be mitigated or avoided by using a single tank filled with solid material that is heated and cooled with air as HTF, see, e.g., Good et al. [5]. This

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## Nomenclature

### Abbreviations

|         |  |
|---------|--|
| AA-CAES | advanced adiabatic compressed air energy storage |
| CS      | calcareous sandstone                             |
| CSP     | concentrated solar power                         |
| DSC     | differential scanning calorimeter                |
| F       | felsic rock                                      |
| HTF     | heat-transfer fluid                              |
| L       | limestone  |
| M       | mafic rock                                       |
| QC      | quartz-rich conglomerate                         |
| S       | serpentine                                       |
| TES     | thermal-energy storage                           |

### Greek symbols

|               |                             |
|---------------|-----------------------------|
| $\phi$        | open porosity (-)           |
| $\rho$        | density ( $\text{kg/m}^3$ ) |
| $\varepsilon$ | packed-bed porosity (-)     |

### Latin symbols

|       |   |
|-------|---|
| $c_p$ | specific heat capacity ( $\text{kJ/K kg}$ ) |
| $A$   | TES cross-sectional area ( $\text{m}^2$ )   |
| $H$   | TES height (m)                              |
| $Q$   | storage capacity (kWh)                      |
| $T$   | temperature ( $^{\circ}\text{C}$ )          |
| $t$   | time (h)                                    |
| $V$   | TES volume ( $\text{m}^3$ )                 |
| $z$   | axial coordinate (m)                        |

### Subscripts

|      |             |
|------|-------------|
| max  | maximum     |
| meas | measured    |
| ref  | reference   |
| $c$  | charging    |
| $d$  | discharging |
| $f$  | fluid       |
| $s$  | solid       |

type of storage system is particularly well suited to AA-CAES because the power cycle uses air as the working fluid.

To be considered suitable for TES systems in CSP and AA-CAES plants, solid materials need to satisfy several criteria, including high values of thermophysical properties such as the thermal conductivity, specific heat capacity, and material density and low values of the porosity, see, e.g., Kuravi et al. [1] and Khare et al. [6]. High values of the thermal conductivity, specific heat capacity, and density ensure good unsteady heat exchange with the air and hence high storage efficiencies. High values of the specific heat capacity and density result in a large volumetric heat capacity and therefore enable compact storage systems. Low values of the porosity imply large values of the bulk density, see Bell [7] and Lee and Rainforth [8, p. 73], and the uniaxial compressive strength, see Hoshino [9] and Lee and Rainforth [8, p. 89]. High values of the uniaxial compressive strength are required to avoid fracture and disintegration of the material, which can lead to an increase of the pumping work, clogging of the storage, and may erode the turbine blades in an AA-CAES plant. Among solid materials that satisfy the above criteria, rocks are considered attractive because they are available at low cost due to their abundance.

A sensible TES system based on a packed bed of rocks was demonstrated by Zanganeh et al. [10] with temperatures of up to  $650^{\circ}\text{C}$ . Rocks are especially attractive for AA-CAES plants whose storage caverns are excavated from rock formations because the storage material is a free by-product of the plant construction. Park et al. [11] presented simulations of an AA-CAES plant with a rock cavern and a TES unit based on a packed bed of rocks. In their simulations, the storage was cycled between temperatures of  $20^{\circ}\text{C}$  and  $685^{\circ}\text{C}$ .

Although rocks are regarded as an attractive material for TES at high temperatures, relevant experimental data on their thermophysical and mechanical properties is relatively limited. Most studies have been performed in a geophysical context and focused on the effects of heating to a specific temperature, see, e.g., Somerton et al. [12] and Bauer and Johnson [13]. Early studies were reviewed by Pfannkuch and Edens, see Appendix A-4 in Riaz [14], from the perspective of using rocks as a storage material up to  $500^{\circ}\text{C}$ . Their review focused on experimental data for the specific heat capacity, thermal conductivity, and thermal diffusivity of rocks and rock-forming minerals. They reported that the thermal conductivity, thermal expansion, and sound velocity decrease with thermal

cycling. Particularly relevant are the cycling studies of Poole [15,16]. In the first study, Poole [15] measured a reduction of the thermal conductivity during three cycles up to  $366^{\circ}\text{C}$  with negligibly small heating rates for limestone and  $537^{\circ}\text{C}$  for granite. In the second study, Poole [16] reported a reduction in the thermal conductivity of basalt after two cycles up to  $600^{\circ}\text{C}$ . Poole attributed the reductions to the release of carbon dioxide by the limestone and the formation of microcracks in the basalt and granite. Pfannkuch and Edens concluded their review by suggesting that granites and quartzitic rocks are suitable for TES.

Riaz [14] reported what appears to be the first dedicated experimental investigation of the suitability of rocks for TES. The uniaxial compressive strength, tensile strength, weight loss, and length change were measured on seven North American rocks (basalt, granodiorite, quartzite, two sandstones, and two limestones) after 3, 10, 30, and 100 cycles between  $100^{\circ}\text{C}$  and  $500^{\circ}\text{C}$  at an average heating/cooling rate of at least  $13.9^{\circ}\text{C}/\text{min}$ . Riaz [14] concluded that because of their higher strength, basalt, quartzite, and granodiorite would be better suited for TES than weaker sedimentary rocks such as limestone and sandstone.

Geiger [17] assessed the resistance to thermal cycling of eight rocks from Switzerland (limestone, Helvetic siliceous limestone, serpentine, dolerite, granite, gneiss, peridotite, and amphibolite). The mass loss and the degree of fracturing and disintegration of the samples were evaluated after seven thermal cycles with 460 h at either  $500^{\circ}\text{C}$  or  $600^{\circ}\text{C}$  with unspecified heating and cooling rates. The limestones were judged unsuitable for TES due to fracturing. The granite showed signs of the formation of microcracks that were attributed to the  $\alpha$ - $\beta$  quartz inversion at  $573^{\circ}\text{C}$ . The serpentine and dolerite showed cracking but no fracturing. The gneiss, peridotite, and amphibolite did not exhibit any visible macroscopic changes. Geiger [17] also investigated two rocks from Jordan (quartzite and basalt) by performing seven thermal cycles with 21 h at  $550^{\circ}\text{C}$ . The quartzite fractured after just one cycle. The basalt did not exhibit any macroscopically visible damage.

Allen et al. [18] presented a comprehensive literature review and investigated rocks of South African origin (gneiss, granite, pegmatite, dolerite, sandstone, hornfelsic shale, and greywacke). The rocks were cycled approximately 950 times between average temperatures of  $350^{\circ}\text{C}$  and  $500$ – $530^{\circ}\text{C}$  at  $2^{\circ}\text{C}/\text{min}$  and assessed in terms of the degree of fracturing and disintegration. They

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