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Thermal strengthening of limestone: monument preservation during fire

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The use of natural rocks in the construction of buildings and monuments predates the use of commercially engineered materials such as concrete. Such building material can be subject to elevated temperatures in the misfortunate event of a fire. In civil engineering, it is generally appreciated that the strength of rock is decreased when it is or has been exposed to elevated temperatures. This is due the formation of thermal microcracks, a result of the thermal expansion mismatch between different minerals in the rock. Even today, fire is by no means an uncommon occurrence and approximately one historic building is lost to fire in the European Union every day (COST C17 2001). A large number of historically significant buildings and monuments are constructed from carbonate material. However, could the paradigm of thermal weakening of limestone construction material be in part, a paradox?

We report new findings on the thermal strengthening of the Solnhofen limestone (Solnhofen, Germany), a carbonate rock traditionally used in construction of building and statues in central Europe. Two types of deformation experiments were performed to investigate: (1) the strength of samples at elevated temperatures (i.e. during fire) and (2) the strength of samples at room temperature after heat-treatment (i.e. after fire). During experimentation, microcracking was monitored by the output of acoustic emissions (AE). Thermo-gravimetric (TG) analysis was also undertaken to measure the mass loss during heating. For the experiments 'during fire', samples were heated to temperatures of 25°, 200°, 400°, 500°, 600°, 650° and 800°C at a controlled rate of 5°C/min and deformed until failure in a uniaxial press at a constant strain rate of 10-5 s-1. For the experiments 'after fire', samples were heat-treated to each 100°C increment up to 800°C, they were then cooled at the same rate and their strength tested at room temperature.

The mechanical data demonstrate that, during fire, the strength of the limestone increases up to 400°C, from 117MPa at 25°C to 215MPa at 400°C. Above 400°C the strength decreases significantly (down to 20MPa at 800°C) and the deformation behaviour becomes increasingly ductile and aseismic. After a fire event, the strength remains essentially constant up to samples heat-treated to 200°C. For samples heat-treated between 300°-700°C, the strength increased by about 60% from the 'as received' (i.e. no heating) sample. However, the sample heat-treated to 800°C saw a significant reduction in strength (down to 25MPa). All of the heat-treated samples deformed in a brittle manner and AE (seismicity) was recorded in each case. TG analysis demonstrates that decarbonation (the decomposition of calcite in the reaction CaCO3 → CaO + CO2) at 760°C, explaining the significant weakening at temperatures above 700°C. The TG analysis also shows that, at 800°C, the sample has lost 35-40% of its mass.

Over the course of history, a significant amount of monuments and buildings were crafted in limestone. Our findings suggest that it may be advisable, although feasibly expensive, to carefully heat-treat them to medium temperatures (300-500°C) in order to strengthen them and prolong their lifespan. Furthermore, in the event of a fire, it is of paramount importance to keep the temperature of a structure below the decarbonation temperature. Furthermore, heating-induced colour changes in limestone (cream-pink-grey-white), as observed in this study, could be used as a proxy for the temperatures previously experienced by a limestone monument or building.