12th International Congress on the Deterioration and Conservation of Stone
Columbia University, New York, 2012

TEMPERATURE IMPACT ON COTTA SANDSTONE

Christoph Franzen,[1] Dana Krause,[2] Heiner Siedel[3] and Bernd Ullrich[3]

[1] *Institut für Diagnostik und Konservierung an Denkmalen in Sachsen und Sachsen-Anhalt e. V., Schloßplatz 1, 01067 Dresden, Germany, tel.: +49 (0)351 48430-410, fax.: +49 (0)351 48430-468, franzen@idk-info.de*
[2] *Fachhochschule Hildesheim, Fachbereich Restaurierung / Hein Restauratorengesellschaft mbH, Schnorrstraße 70, 01069 Dresden, Germany o*
[3] *Technische Universität (TU) Dresden, Institut für Geotechnik, Mommsenstrasse 13, 01062 Dresden, Germany*

Abstract

Fire impact on stone can be regularly observed as a damage in historic building material. Also several monuments built from Cretaceous Cotta sandstone material, a quartz sandstone with minor clay components, did show and partially still does exhibit damage phenomena referred to fire attack. For a better understanding of such phenomena experiments have been conducted in seven different temperatures of 300°C, 400°C, 500°C, 600°C, 700°C, 800°C and 1250°C. First interesting and clearly visible result is that the steady-going development in staining changed unexpectedly towards the final temperature step. Pore size distribution by Hg-porosimetry does indicate an increase in pores larger than 10 µm getting significant at 1250°C. This is proven by data of capillary uptake. Compressive strength tends to increase. USV testing including measurement of Young's modulus show clearly a decrease towards higher temperatures.

XRD shows the breakdown of kaolinite as the main clay component at temperatures > 500°C while in SEM the typical booklet structures stay present as pseudomorphoses. Compressive strengths in wet and dry state of heat-treated samples are significantly different at lower temperatures (⩽ 700° C). At higher temperatures these differences disappear. An explanation for the wet and dry results in compressive strength are clay components which are mainly responsible for the strength reduction in wet state and are proven to be destructed in the material treated with elevated temperature.

Keywords: building stone, fire damage, historic material, sandstone deterioration

1. Introduction

Several historic buildings suffered fire damage in their history. Also lots of sandstone monuments were affected by fire and high temperatures due to bomb attacks during the 2nd world war in Dresden. Some of the fire effects and damages are still observable (Figure 1 to Figure 3). Elbe sandstone is the main building material in Dresden since the 16th century (Siedel 2010a).

Main damages on sandstone as building material, what we focus on here, are fracturing and loss of those surfaces which were directly exposed to the temperature impact. Most often pieces of several cm in thickness lose completely the contact to the stone core and fall apart (Figure 1, Figure 3). Regularly a kind of layering parallel to the surface is visible (Figure 1). Also typical is a red staining of the stone material.

Figure 1. Loss of pieces of several cm in thickness parallel to surface, typical fire damage, Dresden, Palais im Großen Garten.

Figure 2. Fire damaged sculpture of Justitia, Residenzschloss Dresden.

Figure 3. Fire damage on masonry, Lepsius Bau, Dresden.

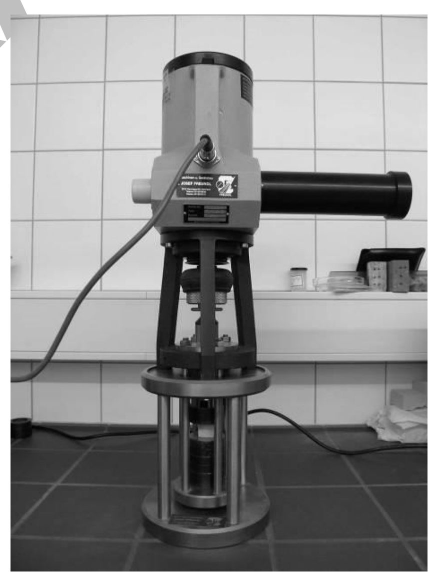

Figure 4. Haft- Zugmessgerät Type F20D Easy, Firma Josef Freundel Maschinen- u. Gerätebau.

Haijpal and Török have previously investigated several sandstone materials typically used as building stone including Cotta Sandstone (Hajpál & Török 2004). They have shown that the colour changes are related to mineral transformations. The most intense colour change is caused by the oxidation of iron-bearing minerals to hematite.

The aim of this experimental study was to get a better understanding of the fire effects especially on Elbe sandstone material. Additional to the heated samples untreated blank samples were dragged through the analysis.

2. Methodology, experimental procedure

For the experimental procedure a Saxonian Elbe sandstone quality 'Cotta' quarried near Neundorf-Rottwerndorf was chosen. The Cotta sandstone material is a quartz sandstone with minor clay components. Cotta sandstone is a fine to medium-grained sandstone with up to 5% of clay (kaolinite, illite). Siliceous bonding is dominant. Occasionally along the bedding planes pore filling cements of clay minerals can be found (Götze & Siedel 2007a). With a particle size in the range of 63 to 200 µm, Cotta sandstone material is a medium to fine grained sandstone. Details of the geological setting are given in Götze & Siedel (2007b). The pore size diameter maximum is approximately 1µm. For comparison pore size distribution as well as other petrophysical data of Cotta sandstone were always determined on the treated and on the untreated samples.

The freshly quarried material was cut into pieces for the different investigations. Size and number of pieces are given within the explanation for each single test procedure. In many times one sample after experiencing the temperature treatment was UV measured, crashed in the strength test and the remains subdivided and used for Hg-porosimetry, XRD and SEM.

Pieces were placed in an oven for ceramics Keramikkammerofen KK 120.16, at HAWK Hildesheim. Samples were treated in seven different temperatures of 300°C, 400°C, 500°C, 600°C, 700°C, 800°C and 1250°C. For each batch five cubes of 40x40x40 mm in size were placed in the oven. Temperature was risen and hold for 120 minutes at the target, than stopped and cooled down slowly. Investigative measures started with the visual inspection and documentation of the samples.

Capillary water uptake was measured on samples 40x40x40 mm (n = 32). Samples were placed in water and the water uptake visible on the outer surfaces was recorded.

From each temperature batch two thin sections were prepared, one parallel and one normal to the sedimentary bedding. Ultrasonic velocity (UV) measurement was tested on samples 40x20x20mm in wet and dry state.

Compressive strength was tested by means of a Haft-Zugmessgerät Type F20D Easy, Josef Freundel Maschinen- u. Gerätebau in Wennigsen (Figure 4). The sample (20x20x20 mm) is placed in a hanging cylinder which is torn upwards with defined force in time. Maximum load was 20 kN.

Pore radii distribution was determined from the remains of the strength test. Sandstone material was analysed by X-ray diffraction (XRD) to detect mineralogical changes. Also SEM inspection was proceeded.

3. Results and discussion

After the temperature treatment the first obvious result are the changes in colour as a more or less steady-going development until 800°C (Figure 5). The pristine Cotta sandstone material of that quality has a grey colour. The 300°C treatment induces a yellow touch in the material. 400°C produces yellow clouds in the sandstone. By the 500°C treatment the colour turns into a pale red. Dark mottles become observerable. With 600°C the red colour becomes more intense, also the dark mottles. It is turning even darker due to the 700°C treatment. Also with 800°C the dark red colour is visible. In terms of temperature difference the step towards 1250°C is huge, so is the colour development: it turns into a grey colour again. The dark mottles nearly get black and dominate the difference in the appearance of the material compared to the untreated.

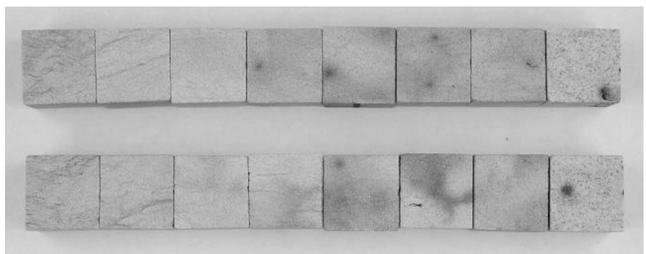

Figure 5. Samples from left to right: untreated sample (grey), 300°C (yellow touch); 400°C (yellow clouds); 500°C (pale red); 600°C (red); 700°C (dark red); 800°C (dark red); 1250°C (grey)

Results concerning the colour development fit in general with correlations done by Haipal and Török (2004). The red colour staining is due to iron oxidation. It has to be noticed that the Fe here is disperse distributed in the sample material. Neither in the thin sections nor by XRD or in SEM Fe-bearing mineral phases are identifiable. But Fe as impureness in constituting minerals is quite usual and in SEM the disperse Fe can be detected.

SEM investigations at different stages of heat treatment (untreated, 600°C, and 1200°C) were focused on cracks, clay particles and glauconite. A significant formation of cracks within the stone fabric could not be found. Kaolinite "booklets" are common in the pore space between the quartz grains. Morphological changes of the crystals cannot be detected at 600°C (Figure 6) and up to temperatures of 800°C, although the structural breakdown of kaolinite in Cotta sandstone occurs already at ca. 500°C according to XRD measurements. The phenomenon of stable platy crystal shapes in kaolin clays at higher temperatures is well-known from investigations on ceramics (Jasmund & Lagaly 1993). At 1250°C quartz and kaolinite crystals partly start to melt, but the platy shape of the former kaolinite grains is still detectable in some places (Figure 7). The appearance of mullite in XRD at this stage can be assigned to novel formation of small, needle-shaped crystals at higher magnitudes in SEM, but might have also taken place in the relics of platy crystals (Jasmund & Lagaly 1993). Novel formed, glassy and porous melting structures at 1250°C (Figure 7) change the porosity towards higher pore diameters and may explain the increase in capillary water uptake as well as the decrease in density. The results of SEM investigations demonstrate the lack of visible changes in microstructures below 1250°C.

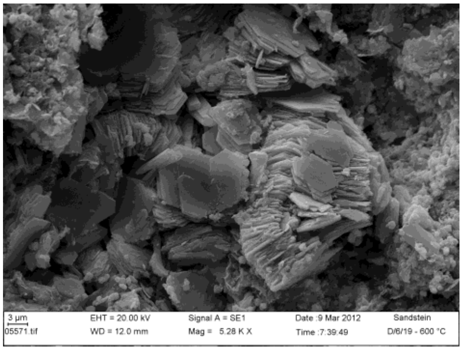

Figure 6. Treated at 600°C, undisturbed booklets of kaolinite

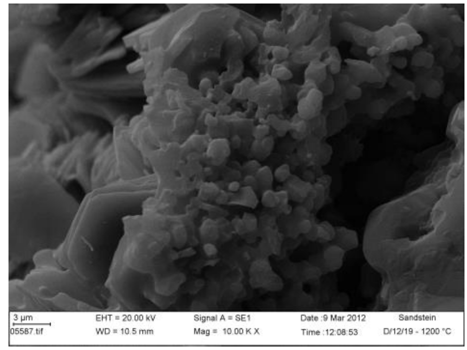

Figure 7. Melting structures and pseudomorphs of kaolinite at 1250°C

According to macroscopic colour changes in the sandstone the colour of glauconite grains in thin sections changes from typical intense green in untreated material to a pale greenish appearance within 300°C over orange, red and brown during the heating stages.

Quartz, kaolinite, and illite are the mineral phases found in XRD diagrams of the untreated Cotta sandstone. Minor glauconite contents can only be detected in the thin sections but not in XRD. Until 400°C the mineral association doesn't change. At 500°C the kaolinite peaks decrease and totally disappear at 600°C. Illite and quartz are stable until 800°C. At 1250°C the mineral content of the sandstone has significantly changed. Beside quartz, cristobalite, mullite and hematite can be found at this temperature.

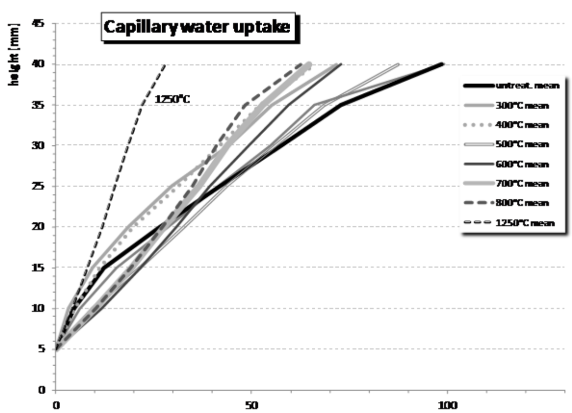

Figure 8. Capillary water uptake is accelerated

Changes in porosity of the sandstone material due to temperature can be deduced from water uptake measurements and Hg-porosimetry data. Results of capillary water uptake are shown in Figure 8. The capillary water uptake does show a tendency of slight changes of the untreated material towards the samples treated by 300° to 800°C. Within this range 800°C samples exhibit faster capillary water uptake. Significant changes towards a more rapidly uptake clearly can be seen after the 1250°C treatment. The diagram does show the mean values for all treatment temperatures. Evaluating all curves in one overflowed diagram may demonstrate that the water uptake of the untreated sandstone samples are statistically in the lower part of the range, where the samples with treatment temperatures between 300° to 800°C do plot. The fastest water uptake of the 1250°C samples is visibly clearly separated.

In Figure 9 data of the Hg-porosimetry is given. Untreated Cotta sandstone material has a total pore volume of about 21.8 Vol.%. Pore size distribution displays a typical monomodal curve with a maximum around 5.4 µm, accumulating nearly 4°Vol.% at that range. This correlates to data from Götze & Siedel (2007a). The curve is displayed in Figure 9 like background. Black lines calculated from the 700°C and 1250°C treatment data exclusively express the difference of the treated material relative to the untreated. Exemplified for most of the 'lower' temperature treatments the difference curve for 700°C is displayed in the upper diagram. Total pore volume is risen to 22.4 Vol.%. The portion of the smaller pores around 0.01 µm is reduced and the contingent of pores in the range of 5 µm to 10 µm is slightly increased. This trend is even more approved in the 1250°C step. The treated material has no significant pores in the smaller range until 1 µm. Also until 5 µm the most portion in that ranges are gone. But there is a huge increase in pores larger than 10 µm. This is the pore range which is relevant for capillary transport.

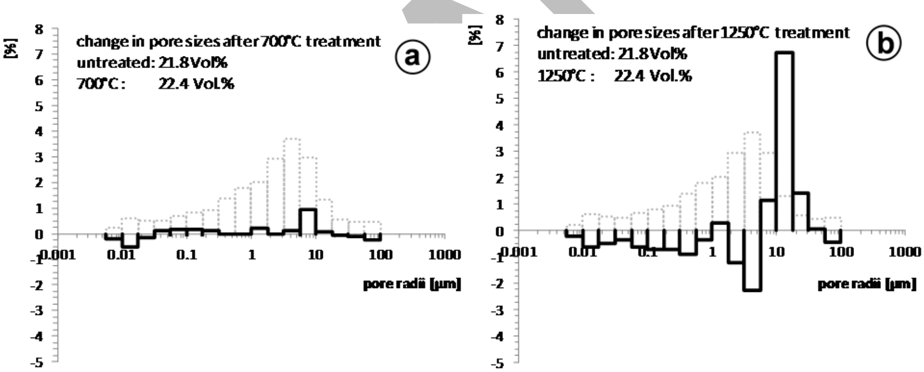

Figure 9. Change in pore size distribution according to temperature treatment. Dotted lines show untreated material, black lines show the difference of the treated material relative to the untreated. a) 700°C, b) 1250°C. Portion of smaller pores is reduced in support of larger pores.

Results of density measurements are displayed in Figure 10. There is a trend towards a reduction in density from 2.0 g/cm^3 to 1.9 g/cm^3. This correlates with the increase in pore volume.

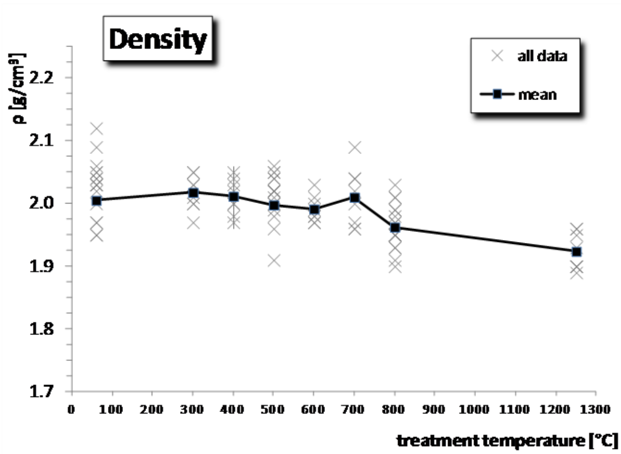

Figure 10. Density development of the sandstone, all measured data and calculated mean.

Compressive strength was determined on four types of samples for each temperature step (Figure 11). Highest Compressive strength was found normal to the bedding on dry samples. Parallel to the bedding compressive strength is about 5 N/mm^2 lesser, which is found on all temperatures. The measurement on wet samples (normal to the bedding) shows a reduction of about 13 N/mm^2 until 700°C. With 800°C and 1250°C the reduction vanishes. A similar correlation can be seen for samples parallel to the bedding: the compressive strength is reduced for about 10 N/mm^2 until 700°C, which cannot be seen for the next two steps. In general it seems that compressive strength shows a tendency to rise with rising temperatures.

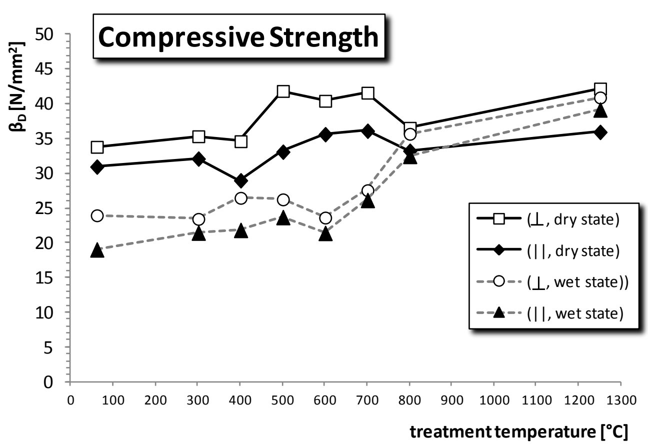

Figure 11. Compressive strength data, parallel and normal to the sedimentary bedding.

The data for the ultrasonic velocity (USV) is shown in Figure 12. Ultrasonic velocity is not changed until a treatment of about 400°C. With each higher temperature treatment USV is decreasing. Parallel to the bedding USV is about 0.3 km/s faster than normal to the bedding. With increasing treatment temperature this difference is reduced to about 0.12 km/s but still traceable.

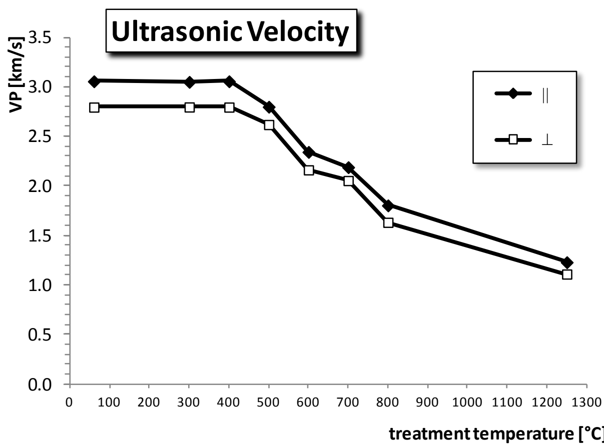

Figure 12. Ultrasonic Velocity decreases significantly (⊥ = normal to bedding, || = parallel to bedding).

4. Conclusions

Cotta sandstone is affected by simple temperature treatment, dependant on the maximum treatment temperature. For the pure eye visible changes are the ones due to iron oxidation resulting in colour changes. In the texture significant changes are not 'visible'. Nevertheless kaolinite suffers breakdown while its platy shapes do remain. The dehydrated metakaolinite changes the material characteristics. The difference in the mechanical behaviour (more 'stiff' and less greasing than kaolinite?) might explain a low increase in mechanical strength above 600°C. The clay contents are the main cause for a lower mechanical strength of wet Cotta sandstone, compared to dry one (Siedel 2010a). With the total decay of kaolinite, the differences in mechanical strength between wet and dry Cotta sandstone reduce permanently up to 800°C, which might be explained by the transformation of kaolinite to irreversibly dehydrated metakaolinite and reduced hydric swelling. A thorough novel formation of the texture including melting processes and glass formation lead to somewhat higher strength again at 1250 °C. The microscopic observations and measurements of technical properties clearly show that the structure of Cotta sandstone in short-range scale, between the single grains, is still stable after temperature impact even at higher temperatures. On the other hand, sandstone objects exposed during fires display regularly cracks and scaling in the scale of some centimetres or decimetres. The observations in our study suggest that this is due to steep gradients of temperature from the fire exposed surface to the depth and the respective thermal expansion rather than to damages of the bonding between single quartz grains. However, a strongly decreasing USV suggests that incipient formation of small cracks between the grains occurs, but seems to be less important for the decay patterns of the whole object than the gradient of temperature. The changes in open space distribution are also detected by the Hg-porosimetry.

References

Götze, J. & Siedel, H. 2007a. A complex investigation of building sandstones from Saxony (Germany). – Materials Characterization 58, 11-12, 1082-1084.

Götze, J. & Siedel, H. 2007b. Methoden zur Provenienzanalyse von Bausandstein aus der Elbtalkreide. – In: Siedel, H.; Franzen, C. & Weise, S. (Hrsg.): Elbsandstein. Beiträge zur Tagung des Arbeitskreises zur Erhaltung von Kulturgütern aus Stein (ARKUS) 2007 in Dresden, 49-57.

Hajpál, M., Török, Á. 2004. Mineralogical and colour changes of quartz sandstones by heat, Environmental Geology, Volume 46, (3), 311-322, DOI: 10.1007/s00254-004-1034-z

Jasmund, K. & Lagaly, G. (eds.) (1993) Clay minerals and clays. Steinkopff, Darmstadt (in German).

Siedel, H. 2010a. The city of Dresden in the mirror of its building stones: Utilization of natural stone at façades in the course of time. - In: Boştenaru Dan, M.; Přikryl, R. & Török, A. (eds): Materials, Technologies and Practice in Historic Heritage Structures. Springer, Dordrecht, Heidelberg, London, New York, S. 137 - 156.

Siedel, H. 2010b. Historic building stones and flooding: Changes of physical properties due to water saturation. – ASCE Journal of Performance of Constructed Facilities 24, no. 5, 452-461.