Fire Damaged Stone Structures in Historical Monuments. Laboratory Analyses of Changes in Natural Stones by Heat Effect

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Abstract

Due to their advantageous properties natural stones were frequently used as building material in historical monuments. From ancient times until quite recently these buildings were also damaged by fire. Although natural stones are non-combustible materials, the fire and heat effect can cause irreversible changes in their structure and mechanical properties, which influence the strength and static behaviour of the stone structures. These changes risk the stability of the entire building. Some fires at the end of 20th century brought attention to the importance of this research topic, since understanding the changes in mechanical properties of natural stones by heat provide additional information for the reconstruction and restoration work of fire damaged historic buildings. The typical forms of alteration of stones exposed to fire are: changes of colour, rounding off corners, spalling and cracking. Laboratory simulated burning with oven-based techniques at 6 different temperatures (150, 300, 450, 600, 750, 900°C) for 6 hours was carried out on 3 types of Hungarian limestones, 3 types of Hungarian and 7 types of German sandstones and 1 Hungarian rhyolite tuff. Quarry fresh samples were drilled and cylindrical specimens were heated under laboratory conditions. Laboratory analyses included the petrographic characterization (thin sections by polarising microscope, XRD, SEM) petrophysical properties testing (specific and bulk density, porosity, water adsorption, duroskop hardness, ultrasonic sound velocity, indirect tensile and uniaxial compressive strength test, colour measuring) at room temperature and at elevated temperatures. The heat resistance of natural stones depends on the type of the stone (sandstone, limestone, tuff, etc.). At the sandstones the major influencing factors are: the type of mineral cement, the amount of cement (grain/cement ratio), the grain size (fine, medium, coarse) and the grain to grain or matrix to grain contacts. The initial porosity, compactness influences the thermal behaviour of limestone and rhyolite tuff. The compact stones show more dramatic change in porosity at elevated temperatures and they are more rigid. A porous and cement-rich stone is more durable and can bear the addition strength caused by thermal expansion.

Keywords: natural stone, historical monument, fire, heat effect, petrological and petrophysical analyses

1. Introduction

Nowadays natural stones as structural elements are found mostly by historic monuments, the application of natural stones in modern architecture is mostly as coating. In Europe natural stones were often used as building material due to their advantageous properties and numerous historic buildings have been built from stone. They have natural stones also in their structures (cope, vault, column, pillar, stairs, access balcony, lintel, bracket, etc.) and also by non load-bearing parts (embellishment, floor-plate). The fine-grained workable stones were popular as raw material of trim-stones, frontal ornamentations or sculptures. For load-bearing, structural elements (cope, vault, column, pillar, stairs, access balcony, lintel, bracket, etc.) mostly the hard, compact types were applied.

Our old towns and stone buildings in Europe have been frequently damaged by fire from historic times till present. In the stone building material the fire causes irreversible changes, which influence the strength and static behaviour of the whole monument. Unfortunately also nowadays becomes heavy fires, which unsafe either whole town quarters. Some fires at the end of the 20th century brought attention to the severe damage that fires can cause to historic buildings and their building stones. As some example the followed fire incidents by historic monuments can be mentioned without requiring completeness:

- in England York Minster (1984), Hampton Court Palace (1986), Uppark House (1989), Windsor Castle (1992), St. Michaels Church in Newquay (1993);
- in Sweden: Katarina Church, Stockholm (1990);
- in Denmark: Odd Fellow Palace, Copenhagen (1992);
- in Portugal: Chiado, Lisbon (1988)
- in Italy: Theatre “La Fenice”, Venezia (1996), Cathedral of Torino “Sacra Sindone”, Torino (1997);
- in Austria: Redoutensal, Hofburg Palace, Vienna (1992);
- in Hungary: St. Michael Church, Budapest (1998).

Till the end of the 20th century mostly only fire resistance of wood, steel and concrete have been investigated. Due to prefabricated buildings the studies have been limited to the role of stone as an aggregate for concrete. The restoration works of fire damaged historic monuments built of natural stone in the last century animated the previous researches on the effects of fire on monumental stones and they have mainly focussed on morphological changes taking place on stone surfaces such as cracking, scaling (Kieslinger, 1932; BRE, 1945) or analyses of colour changes (Chakrabarti et al., 1996). In some cases few mechanical properties of fire-damaged sandstones or heated specimens were also measured (Chakrabarti, 1993; Allison and Goudie, 1994; Hajpál and Török, 2004). In Europe sandstones were very popular as building material. Their sensitivity to heat were shown by oven tests under laboratory conditions through few researcher (Török and Hajpál, 2005; Hajpál, 2002; Hajpál, 2006). This and also the investigation for the rebuilding of the Dresdener Fauenkirche (Hajpál, 2002b) also provide valuable information on the thermal behaviour of sandstones. The mineralogical and textural changes have been also published in detail.

First the traces of deterioration by fire are shown in this paper, then the results of petrological and petrophysical laboratory tests made on different stone type samples are demonstrated. In the future the research will focus on the statical analysis of fire damaged stone structures with the help of a computer model. The analyzing the statical behaviour and load carrying capacity of structural part will be simultaneously subjected to normal loading and high temperature.

2. Traces of fire damage in stone structures

The burning circumstances (e.g. one-sided or more-sided heating, homogenous or heterogeneous heat, the size of the burned stone, velocity of heating, the maximum burning temperature, stone type and its characteristics) influence the changes and the degree of damage caused by fire at the natural stones. It was established that one-sided and quick heating is much more disadvantageous than more-sided, slowly and moderated. Thin elements like plates become warm sooner than blocks, that’s why their suffering is also less than by blocks. By small and localized fires generally didn’t generated much heat and their damaging effect is limited to surface effects and soiling of the surface by smoke. Out of accordance the large and widespread fire generates more heat and issue significant changes at the physical-chemical properties of stone structure.

By the natural stones the decay on effect of heat is a form of physical and chemical changes in stone. By heat effect the changing of the inner stone structure and at the rock constituent minerals induce the altering the character of the stone and the appearance of macroscopic decay.

The typical traces of deterioration by fire are: changes of colour on stones, rounding off of corners by blocks, spalling parallel of surface and cracking.

2.1 Colour change

The colour changing is the most visible effect at natural stones by fire or high temperature. But we have to be careful, because the cause of a colour changing can be an other impact, e.g. simple weathering too!

Heat causes the development of a pink or reddish-brown colouration in brown or buff-colour, which corresponds to the dehydration of iron compounds. This redding isn’t observable at white or grayish stones, which are relatively free from iron oxide. The colour changes begin about at a temperature of 200-300°C at most rocks. By a fire test of big stoneblocks a sharp boundary was noticeable between the heated, red-coloured stone surface and the unaltered stone behind. The width of this zone, the red burned crust was about 2-3 cm, which certainly depends on burning circumstances (degree, distance and duration of fire).

By some stones, which contain a very small amount of organic substance, but it can’t be seen and seldom found in analysis, the organic matter begins to turn into coal at about 500°C and as an effect the grey colour covering the red one. At an increased temperature the carbon is burnt away and the original colour is visible again.

2.2 Cracking, spalling

Cracking, shattering, scaling, spalling are other significant kinds of decay of stones by burning. These can completely destroy the richer carved forms of architecture (Fig.1.a) and damages the smoother forms. Often they are so badly spoiled that a replacing for new ones is necessary.

Figure 1: a) Fire damaged capital of St. Michael Church (Budapest, Hungary) b) Heat effect related spalling of a sandstone window, Monastery in Lobenfeld (Germany)

Heat effect related spalling is a typical form of fire damaged sandstones. Fig.1.b shows a window of the Monastery in Lobenfeld, in Germany, where the stone was quickly heated from one side, but it was still cold in its inner parts. During the fire the process of scaling is permanent. The surpassing of strength by the stone forces that bursting of the hot outer part and the rock peels like an onion. In the simplest cases the bursting of occurs in shells parallel to the surface: a sphere will burst in spherical calottes, a column in cylindrical shells.

2.3 Breaking, rounding off the edges

Rounding off the edges is observable if there is an edge and the heat can work from two sides. This form of decay is regularly to seen on steps, edges of pillars and window-heads.

Where single parts are jutting out of a plane (Fig.1.a) breaking is typical decay (e.g. scaling of bosses just to the depth of groove, the bursting of the ribs of channelled columns, etc.). The abutting part heats up more quickly and burst off easier, because the stresses find the way out more quickly. Often additional notch effects arise, if the jutting part is sharply divided from its neighbourhood. The form of bursting will influence by all kinds of carving in stones. At a very long heated construction (e.g. a door post or the longstep of a staircase) by fire effect the length will be subdivided by means of small transverse cracks into divisions a range of pillow-formed surfaces (BRE, 1945). By inhomogeneous stones the texture (e.g. layers of mica, lamination, fine capillary cracks) will heavily influence the form of decay.

3. Studied stones

Some natural stone types frequently used in historical monuments were taken into the experiments. Three Hungarian limestone types, three Hungarian and seven German sandstone types and one Hungarian rhyolite tuff were chosen for the investigation (Tab.1.). The selected stone types showed a wide range of their feature (colour, grain size, cement type, age, rock constituent minerals, porosity, strength). This compositional variation enables us to achieve a better understanding of how such properties influence the behaviour of natural stones under heat.

Table 1: A summary of the investigated stone types

	Name	*Colour*	*Grain size*	*Cement type*	*Age*
Sandstone	*Balatonrendes (V)*	*reddish*	*fine*	*ferruginous-clayey*	*Permian*
	Ezüsthegy (E)	*white*	*fine*	*kaolinitic*	*Oligocene*
	Rezi (R)	*greenish*	*medium*	*jarositic*	*Pannonian*
	Cottaer (C)	*greyish*	*fine*	*kaolinitic-illitic*	*Cretaceous*
	Donzdorfer (D)	*ochre*	*fine*	*ferrigenous clayey*	*Jurassic*
	Maulbronner (M)	*reddish grey*	*fine*	*clayey*	*Triassic*
	Pfinztaler (Pf)	*greyish red*	*medium*	*chlorite*	*Triassic*
	Pliezhausener (Pli)	*yellowish white*	*medium*	*dolomitic*	*Triassic*
	Postaer (Po)	*off-white*	*coarse*	*siliceous*	*Cretaceous*
	Rohrschacher (B)	*grey*	*fine*	*calcareous*	*Miocene Molasse*
Limestone	*Tardos (T) (compact)*	*red*	*fine*	*micritic calcite*	*Jurassic*
	Süttő (travertine)	*creamy*	*fine*	*micritic calcite*	*Pleistocene*
	Sóskút (oolitic)	*yellowish white*	*coarse*	*sparitic calcite*	*Miocene*
Tuff	*Egertihamér*	*grey white*	*fine-coarse*	*volcanic glass*	*Miocene*

4. Methods

For the simulation of the effect of fire a simplified heating method was used, because of the complexity of the fire processes and the lack of knowledge of the behaviour of stone material by heating effect. Cylindrical specimens with 40 mm diameter were prepared from the stone blocks and these were heated in a homogenous way in an electrical oven at 6 different temperatures (150, 300, 450, 600, 750, 900°C) for 6 hours. Warming up took 1 hour, and after controlled heating the specimens cooled down slowly in the oven. The samples were tested before and after the heating processes carried out at each temperature.

The mineralogical composition of the samples heated to the different temperatures was determined by X-ray powder diffraction (Siemens D500) and by differential thermal analyses (MOM Derivatograph, 20-1000°C). Textural and mineralogical alterations were visualized under polarizing microscope in thin sections and by scanning electron microscopy (Cambridge Stereoscan). The petrophysical analyses included the measuring of specific and bulk density, porosity, water adsorption, duroskop hardness (Duroskop, Bauart von Leesen, Hahn & Kolb), ultrasonic sound velocity (Ultrasonic Tester E46). Indirect tensile strength test (MC 100) and uniaxial compressive tests (DRMB 200) were also made. The colour changes were tested with CIELAB method (Minolta CM-508i).

5. Results

5.1 Petrological analyses

Changes of the texture and inner structure are the results of the mineralogical analyses. Perforce of these the increasing in porosity, the disappearance of minerals or formation of new mineral phases and the colour change were observable.

By sandstones as major effects the transformation of α-quartz to β-quartz (580-595°C) and the formation of micro-cracks at quartz and feldspar boundaries above the 600°C heating temperature were detectable. At higher temperatures (above 750°C) micro-cracks develop also within the crystals. Clay minerals and phyllosilicates are more sensitive to heat and show several transformations at elevated temperatures. In the ferruginous Balatonrendes sandstone the changing of the iron-hydroxide and the kaolinite was shown. The kaolinite structure collapses completely at around 550°C. Illite-smectite mixed layer clay minerals are more stable than kaolinite. Illite can be still detected at 900°C, although it looses the structural water (dehydroxylation) at 553°C. In Ezüsthegy sandstone the micas iron contents oxidize and the clayey cement comes away from the pore wall and hereby the mineral become dark. The structure of kaolinite mineral partly collapse after 750°C the, but thanks to the extremely large crystal size it is recognizable yet. Besides mineralogical changes a colour change may also indicate the transformation of a clay mineral. For example glauconite will be orange (at 450°C) and finally will become brownish red (at 900°C). Another example is chlorite, which shows a colour change from green (at 22°C) to yellow (at 900°C) most probable due to the oxidation of iron (II) to iron (III). In the Rezi sandstone the jarosite mineral changed its colour to yellowish brown by heating and it modified to hematite above 450°C. Kaolinite and chlorite first coloured by increasing the temperature then ruined additionally in the inner structure and in quartz cracks occurred (Fig.2.a). In calcareous Rohrschacher sandstone at 750°C the structure of the calcite collapse and at 900°C the calcite and dolomite decompose to form CaO and MgO (Fig.2.b). Leaving the samples at room temperature induce the appearance of a new mineral phase, portlandite $Ca(OH)_2$. The formation of portlandite is associated with volume increase and leads to the disintegration of heated cylindrical samples.

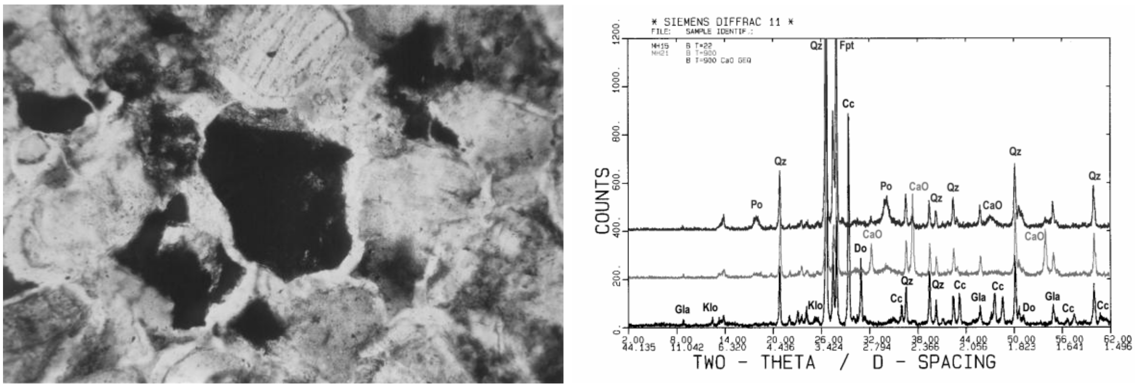

Figure 2: a) Micro-cracks at grain boundaries at 600°C in Rohrschacher sandstone (thin section photograph) b) XRD graphs of Rohrschacher sandstone. (calcite–Cc, dolomite-Do, portlandite-Po, quartz-Qz-, Feldspar-Fpt, chlorite-Klo, glauconite-Gla)

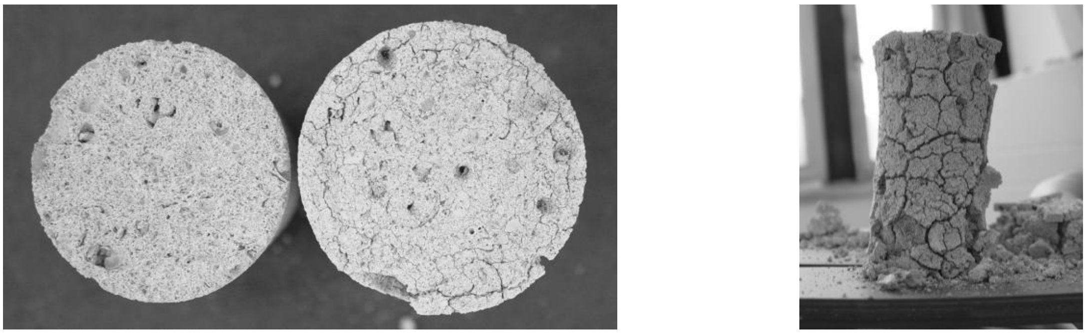

Figure 3: a) Volume increase at Sóskút coarse limestone on 900°C compared to unburnt state b) Sóskút coarse limestone sample after heating on 900°C

At limestones due to calcination processes in the carbonate minerals the major changes took place at 450°C and above. At 750°C the structure of calcite collapsed and at 900°C calcite and dolomite was not possible to detect; however after leaving the samples at room temperature for two hours at about 45% relative humidity a new mineral phase, portlandite was detected. This is a reaction product of air humidity (water) and CaO and associated with a volume increase of 20% in average (Fig.3.a) and leads to the disintegration of cylindrical specimens. In Tardos limestone a thin film of iron oxides cover the calcite crystals in some places and this degrades with the heating. In the Süttő travertine the calcite crystals are very rough, which show that the deposition was very quick. Thermal cleavage, inter-granular crackings and incipient surface dissolution of s occurred at the effect of heat. In Sóskút coarse limestone the heating makes small inter- and intragranular cracks arisen, which occur decided porosity increasing at elevated temperature. In Egertihamér rhyolite tuff bentonite flakes cover the surface of lithic clasts as a thin film. Above 750ºC this is not yet recognizable.

5.2 Petrophysics

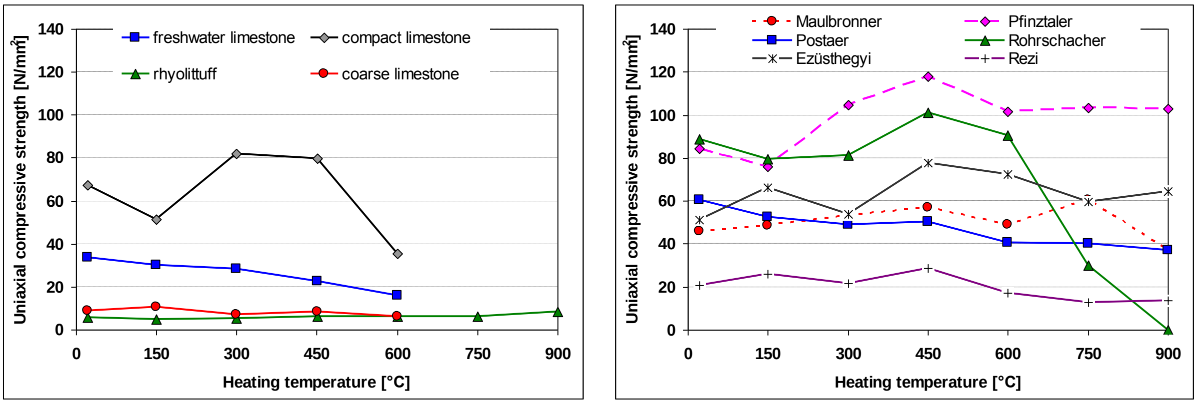

Figure 4: Uniaxial compressive strength values as function of heating temperature at different stone types a) Hungarian limestones and rhyolite tuff b) Hungarian and German sandstones

The limestone samples were sensitive at the heating. On the compact limestones specimens small hairline cracks arose already after at heating on 450°C and over the 600°C heating temperature the samples exploded. These specimens faded at the elevated temperature (750°C). The travertine samples grown dark till 450°C and smelt foul due to organic matter content, but after this there also paled. These specimens survived the heating, but some hours after the test the CaO had reaction with the air moisture and due to nascent portlandite and the volume increment the samples crumbled. The coarse limestone samples also stand out the effect of heat at 750°C and 900°C, but they have falled into dust soon (Fig.3.b). Some reports (Chakrabarti et al. 1996, Török and Hajpál 2005) mention this process by high temperature tests of calcite containing stones. The heating did not result similar problems at the sandstones and the rhyolite tuff samples.

Fig.4. shows the results of the compressive strength test as function the heating temperature. It can be observed, that the heating does dot causes a decrease in the strength in all cases. The Balatonrendes and Ezüsthegy sandstone and also the Egertihamér rhyolite tuff has higher strength after the heating at 900°C as in the beginning state before heating. The limestone types lost their strength not promptly but only at elevated temperature.

The colour changing was detectable by eyes, but for the correct determination instrumental testing (CIELAB method) was also used. The colour modification of stone types was different (Fig.5.). The dark grey colour of travertine samples at elevated temperature and the nascent hum indicates to organic matter content.

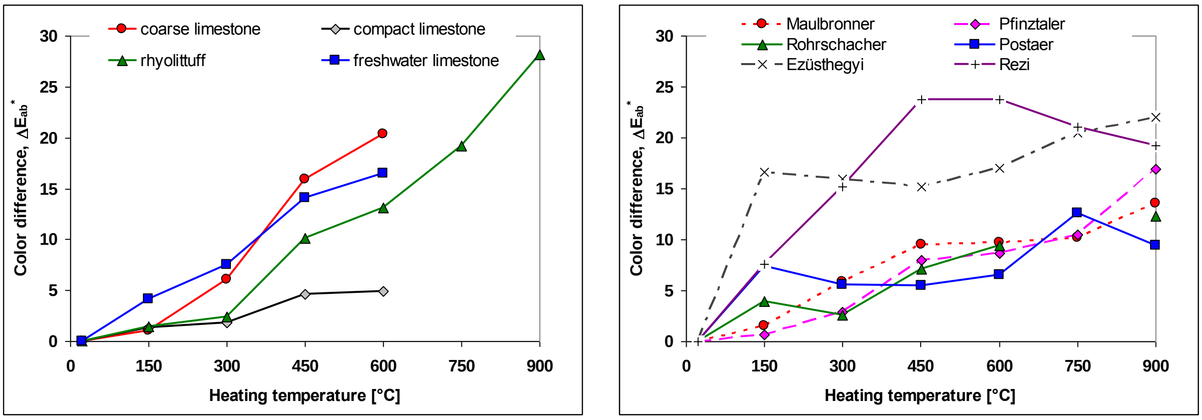

Figure 5. Colour difference values as function of heating temperature at different stone types a) Hungarian limestones and rhyolite tuff b) Hungarian and German sandstones

6. Summary, conclusion

Fire and elevated temperatures cause changes in the inner structure and in mineral composition of natural stones. These alterations modify petrophysical parameters too. These changes were mainly observed at elevated temperature. Some mineral transformations cause a volumetric increase, or different thermal expansions initiate cracks in stone. This effect can be responsible for the increase in porosity and the decrease in strength in some cases.

The results of these simulated fire tests have shown that the heat resistance of natural stones depends on the type of the stone (sandstone, limestone, tuff, etc.). At sandstones the major influential factors are: the cementing mineral, the amount of cement (grain/cement ratio), the grain size (fine, medium, coarse) and the grain to grain or matrix to grain contacts. The clay containing stones are more resistant to heat than the calcareous ones. The most fire resistant types are the fine-grained, matrix-rich sandstones and the rhyolite tuffs. The initial porosity, compactness influences the behaviour of limestone and rhyolite tuff under elevated temperatures. Limestones are more heat sensitive than sandstones or rhyolite tuff. In limestones hairline cracks could develop and following the heating experiment exploding or disintegration and loss of strength were observed after exposing the specimens to elevated temperature. By heating some sandstones and rhyolite tuff can be more stiff and durable, an adverse change takes place. The compact stones show more dramatic change in porosity at elevated temperatures and they become more rigid. Porous and cement-rich stone is more durable and bear addition load caused by thermal expansion. The silica cemented, ferruginous or clayey stones are less sensitive than the carbonate-cemented ones, which shows signs of disintegration at higher temperature.

When natural stone structures are considered, it is observed that stone columns and pillars are more sensitive than walls. The cross-section can be significantly decrease and the structure might collapse due to fire.

In the future besides testing small test specimens under laboratory conditions the computer modelling and testing of entire stone structures in a large oven are planned. The results of this research could be applied in many fields of engineering. It was observed that the use of cold extinguishing water at the fire fighting is very harmful for the stone parts of the historical monuments and it can cause damages in the stone structure, which can lead to stability problems.

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