Investigations on former stone conservations at the Kapellenturm, Rottweil

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ABSTRACT

The church tower "Kapellenturm" and its nave, located in the historic center of Rottweil, the oldest city of the federal state of Baden Württemberg in Germany was built from 1330 to the end of the 16th century. The tower was built with local, clay–rich sandstone of the middle Keuper (Stuben sandstone and clay-rich, Schilf sandstone). During the 18th and 19th centuries major interventions to the building fabric were already necessary due to structural safety problems and deterioration of the sandstones. While at that time local Schilf sandstone was used for stone replacement work, later in the 1950´s the balustrades were replaced using limestone (Muschelkalk) from Crailsheim) and a fine-grained Kordeler Buntsandstone were used for replacement in the masonry.

In the early 1970`s chemical products such as diluted hydrofluoric acids and fluates were applied in stone conservation of the clay-rich Schilf sandstone. At the end of this campaign the first hydrophobic treatment was carried out. In 1986 the hydrophobic treatment was repeated with diluted Wacker 290S.

In 2008 serious decay of the Schilf sandstone in the upper octagon area of the tower was detected. Large - sized scaling, massive discoloration and the formation of new cracks necessitated a new intervention. Mineralogical and chemical investigations were carried out to understand the mechanism of building stone decay and the influence of the former stone conservation products applied in this case.

Microscopic investigations showed highly corroded feldspar and clay minerals and the formation of fluorite crystals on the stone surface as a result of the former application of fluoric acid products for stone conservation. The gray and brownish discoloration of the Schilf sandstone surface also led back to this treatment.

Capillary water absorption measurements indicate a strong variation in quality of the hydrophobic treatment, according to the different sandstone types used and their conservation status.

Keywords

Stone strengthener, fluoric acid, Schilf sandstone, Kordeler sandstone, hydrophobic treatment.

1. Introduction

The work of the so called Kapellenturm and its church at Rottweil began around 1330. Local sources of Stuben sandstone and Schilf sandstone were used for building up masonry and stone carver works. The Kapellenturm is divided into three sections: the base layer consists of a quadratic area with several portals and two staircase towers (see Figure 1). The array of sculptures consists of 7 tympana and 27 outstanding sculptures.

Above the base layer follows the central block, topped by the octagon, which was built at the end of the 15th century. While the central block of the steeple still shows a massive construction, the octagon was built in a slender design. Large windows, profiles and structural decorations form the wall area. Due to stability and decay problems according to the clay-rich Schilf sandstone massive repairs were required.. First actions were recorded around 1815 – 1819 including the replacement of the balustrade. Later in 1882 – 1896 again the replacement of many cut sandstones with serious decay was necessary.

Figure 1 Historic view of the Kapellenturm at Rottweil (around 1930, Bildarchiv Marbach).

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In the 1950´s the balustrades were replaced once again, this time using Muschelkalk from Crailsheim for replacement. Starting with the 1960´s, fine–grained Kordeler sandstone from Trier was used for stone replacement. From 1966 – 2001 continuous work on stone conservation and restoration took place in the Kapellenturm [1].

The damage progress and the visible changes of the Schilf sandstone surfaces (e.g. discoloration, bleaching) at the octagon area in the last decades suggested some relationship to the former stone conservation products. Studying some old promotion materials of the manufacturer lead to doubts in the effectiveness and compatibility with sandstones, poor in carbonate, but rich in clay-ferritic grain cement.

2. Early stone conservation

Around 1970 a chemical treatment was applied on the Schilf sandstone at the octagon area. For chemical cleaning of the stones surface and pre - fortification of the sandstone different "Hermetique" products like Hermetique–sandex were used, then additional Hermetique products (Hermetique conservans, Hermetique KS44) in appropriate dilutions were applied for strengthening of the sandstones to adequate depth. Today only information about its chemical compositions is available. For example, Hermetique sandex was described by the manufacturer as a "special combination of fluoric acids", but fluates and waterglass were also used [2]. Finally, a hydrophobic treatment with Hermetique silicon was deployed. The sales promotion of the manufacturer promised strengthening due to the following chemical reaction process: Limestone + hydrofluoric acid = calcium fluoride + CO_2. The manufacturer described that calcium fluoride is insoluble in water and shows a hardness like quartz. Even silicate minerals are slightly soluble in hydrofluoric acid and also stone layers depleted in carbonate should be reinforced. Dissoluted quartz should be accumulated between the loose mineral particles and gapfilling [2]. Further on in 1986 the hydrophobic treatment was renewed using a diluted solution of Wacker 290S.

3. Damage and preliminary investigations

In 2007 several pieces of falling stones lead to mapping of building phases, material mapping and damage mapping. In the octagon area different types of sandstones and limestones were built in over the past centuries: Stuben sandstone from Dettenhausen, limestone from Kirchheim and Crailsheim, Savonnieres – limestone from France, green Schilf sandstones of local origin and Kordeler sandstone from Trier [3]. The Kordeler sandstone from the upper Buntsandstone, light – yellow to grayish in colour, fine - grained and with small, dark stainings of iron-manganoxides is located around Kordel close to Trier. On average the mineralogical composition consists of 47% quartz, 42% rock fragments, 8% feldspar, 3% glimmer minerals and less than 1% accessories. Clay minerals, mostly kaolinite cemented the quartz and feldspar grains. The feldspar shows diagenetic dissolution and the quartz grains are often in sutur - contact. Kordeler sandstone is classified as well resistant to weathering [4].

The local Schilf sandstone is a fine–grained, green to greyish-green, homogenous and mainly clay-rich bound sandstone. On average the Schilf sandstone contains a high amount of rock fragments, feldspar and quartz. The grain cement consists of clay–ferritic covering around the coarser grains, silicic cements are rare. Most of the Schilf sandstones are reasonable to less resistant to weathering.

Most of the new damages at the octagon level of the Kapellenturm are limited to the original cut stone and replacement materials from 1882. The stone conservation treatment of the 1970s plays an important role on the decay:

- Contour scaling and flaking
- Brownish and white discoloration of the greenish sandstone surface
- Development of cracks and partly fragmentation
- Staining due to hydrophobic treatment, especially on the Kordeler sandstone

Samples from the Schilf sandstone, showing serious decay, were investigated (see Figure 2 – 4).

Figure 2 Development of cracks (partly filled with cementitious materials) and discoloration at the stone surface, local green Schilf sandstone (photograph by Frank Eger).

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Figure 3 Contour scaling and development of cracks in the Schilf sandstone, white and brownish discoloration, note the original green color of the sandstone.

Figure 4 Staining due to hydrophobic treatment, Kordeler sandstone (photograph by Frank Eger).

4. Methods of investigation

The mineralogical composition of the different Schilf sandstones were analyzed by XRD spectrometry (Bruker AXS D8, Cu–Kα–radiation, SOL-X detector). Compositional changes at the stone surface were investigated using a SEM/EDX system (Camebridge CS4). The samples were sputtered with a thin layer of gold.

Soluble salts were detected by ion chromatography (Dionex ICS 1500, sodium-hydrogen-carbonate - eluent).

5. Results

5.1 Microscopic investigations by SEM - EDX

Microscopic investigations show at the surface and some millimeters in depth a coating of the rock forming minerals with Si–rich gels. Most of them do not show any cracks from shrinkage, like gels deposited from modern silicic acid esters do (see Figure 5). As a result the stone surface was condensed and small cracks due to the development of higher tension or stress occurred. Below this dense and hard crust the sandstone shows higher porosity and loss of adhesion of the clay–rich grain structure.

Etched and severely corroded feldspar minerals with small, cubic and octahedral fluorite are the result of the stone conservation treatment of the 1970s using fluates (see Figure 6, 7).

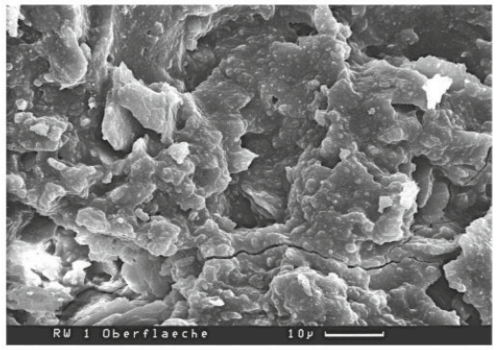

Figure 5 Surface of the Schilf sandstone of sample RW 1, coated with SiO_2 – gels, probably hardened from waterglass. Note the highly compacted surface and the development of cracks (not from shrinkage).

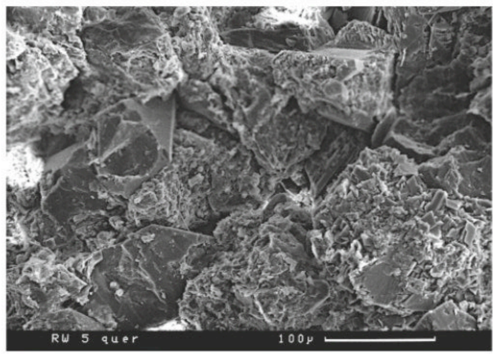

Figure 6 Etched and highly corroded feldspar minerals, influence from the application of fluoric acid for stone cleaning and strengthening.

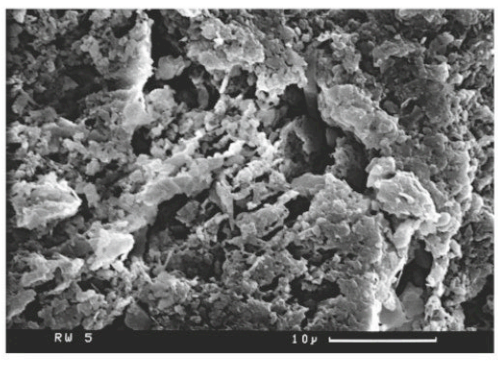

Figure 7 Etched structure of the clay-rich sandstone, increase of porosity due to silicate mineral solution processes.

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In carbonaceous natural stones the fluates or fluoric acid in aqueous solution are reacting with calcium carbonate to fluorite (CaF_2). The manufacturer of the "Hermetique" products promised a long – lasting reinforcement of any kind of carbonaceous and even siliceous sandstone. In fact, the mineral surface of the clay minerals and of the feldspars have been etched and the rarely formed fluorite rests on the surface in single crystals showing no reinforcement (Figure 8).

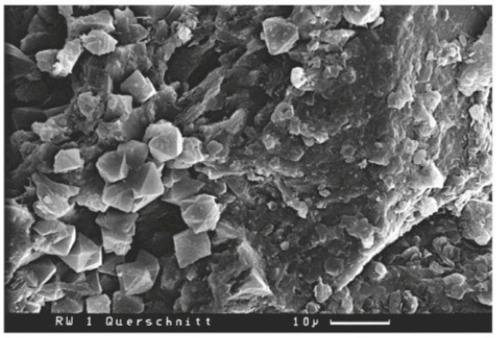

Figure 8 Small octahedral fluorite crystals growing on the clay mineral structure of the Schilf sandstone. Etched quartz grain on the right side.

But a strong discoloration of the green sandstone to a grayish colored surface occurred. Additionally Fe^{2+} - ions from iron bearing clay and chlorite minerals were dissolved in the more acidic pore solution and caused a brownish discoloration due to the formation of iron oxides at the stone surface (see Figure 9). Together with the siliceous gels precipitated from waterglass, which was applied in different concentrated solutions a dense and discolored crust with a medium thickness of 1 – 2 cm was formed.

Figure 9 Brown and grayish discoloration of the stone surface, Schilf sandstone.

5.2 Detection of soluble salts

The results of the eluted, solulable salts of the Schilf sandstone samples showed unusual, high concentrations of fluoride ions in the eluate, which are a consequence of the Hermetique treatment (Table 1). In the almost carbonate–free Schilf sandstone only less Ca–ions are being available from the dissolution process of Ca–rich feldspars. Certainly alkali – ions (Na+, K+) are available due to the acid attack from HF to albit–rich feldspar, alkali feldspar, chlorite- and clay minerals. Further sources of alkali ions to be considered are fluates and waterglass from the treatment. In addition to the soluble fluorides only higher amounts of sulfates are present (mainly gypsum), accumulated close to the surface from deterioration and weathering processes.

Table 1 Concentration of anions in wt.-%

Sample	F^-	Cl^-	NO_3^-	SO_4^{2-}
RW P1	0,20	<0,01	<0,01	0,04
RW P3a	0,05	<0,01	<0,01	0,02

5.3 Capillary water absorption

The preliminary assessment by determination of the water absorption coefficient showed an obvious hydrophobic behavior of the stone surface. The non-destructive measurements were done onsite with a graduated glass tube (Karsten tube) as a function of time. For calculation of the absorption coefficient w an Excel spreadsheet Calkarow 3.2 based on the algorithm of Wendler [5] was used (Figure 10).

Additionally some sandstone samples were taken by drilling and investigated in the laboratory according to DIN EN 1925 [6].

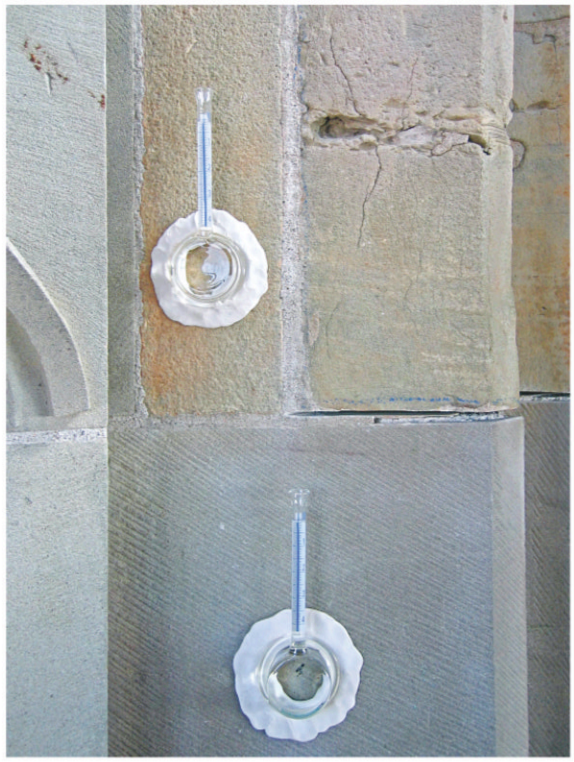

Figure 10: Determination of capillary water absorption by Karsten tube measurements. Upper part: Schilf sandstone, lower part Kordeler sandstone.

Onsite the depth of the hydrophobing zone was tested by wettability. In average a hydrophobic zone of about 2 mm in depth was detected. The remaining quality of the hydrophobizing (finally applied in 1986, Wacker 290S) was different, dependent on the type of sandstone. The Kordeler sandstone, used for substitution in the 1960s showed still good results. Its water absorption coefficient was in average 0.3 $kg/m^2h^{-0.5}$. But the different Schilf sandstones from various restoration phases showed higher values of about 0.5 $kg/m^2h^{-0.5}$ on average. The evaluation of the effectivity of the hydrophobizing was carried out according to the assessment of the WTA [7]. In agreement with the WTA scale of 1-5 a retreatment of façades impacted with wind-driven rain is necessary by reaching a critical average value of w = 0.5 $kg/m^2h^{-0.5}$. A highly effective hydrophobizing should have

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a w – value < 0.1 $kg/m^2h^{-0.5}$ [8]. Clay–rich sandstones like Schilf sandstone are critical respective to the effectiveness, because quartz-rich sandstones show a high amount of free silanol groups at its quartz surfaces. In contrast clay minerals exhibit silanol groups only at their rims, which can react with siloxanes. The polysiloxan films therefore only stretch like canvas from clay particle to clay particle [9].

6. Conclusions

The results of the mineralogical investigations on the Schilf sandstone from the Kapellenturm at Rottweil indicate failure of the former stone conservation in the early 1970`s. The application of diluted hydrofluoric acid in combination with fluates or water glass did not improve the strength of the Schilf sandstone. On the contrary, the structure of the Schilf sandstone was seriously damaged and silicate minerals were etched and partly dissoluted. As a result, many voids evolved. The formation of dense and discolored crusts showing many cracks and partly contour scaling is widely developed in the remaining original Schilf sandstone. Therefore, it is very difficult to hinder the deterioration and preserve the actual status of the sandstones.

The results from capillary water absorption measurements indicate varying quality of the hydrophobic treatment, according to the different sandstone types and conditions of conservation status. Further investigations on the impact of multiple water repellent treatments with modern polysiloxanes (e.g. influence on water vapour diffusion behavior, depth of penetration, discoloration) are necessary. At the end of the new restoration campaign it will be necessary to decide, whether a second repetition of hydrophobizing should be carried out or abstained. Currently a patchwork of none – treated, new replacement sandstones, new repaired joints, poorly water repellent (remaining original Schilf sandstones) and highly water repellent sandstones (Kordeler sandstone) exists.

7. Acknowledgements

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