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Cover image: The front door of the Paisley Technical College building, now University of the West of Scotland. T.G. Abercrombie, architect 1898. Photograph and cover design by T. Howind.

ARTIFICAL AGEING TECHNIQUES ON VARIOUS LITHOTYPES FOR TESTING OF STONE CONSOLIDANTS

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Abstract

This paper focuses on a series of ageing tests performed in the frame of a wider study on the use of innovative consolidants for various architectural stone types. The tested lithotypes can generally be broken down into two categories: silicate (quartz sandstone with a clayey matrix) and carbonate (porous detrital limestone and marble). The predominant deterioration phenomenon of all these stones on-site is loss of grain cohesion and the formation of micro cracks. Thus, the emphasis lies on reproducing this key-deterioration effect in every lithotype. An additional effect to be studied for porous limestone is the formation of a gradient of compactness within the specimen, mimicking a crust on loose substratum. The ageing progress was evaluated by the methods of determining changes in ultrasound velocity and water absorption coefficient by capillarity. At critical stages the micro defects created are analysed by polarizing light and scanning electron microscopy on petrographic thin sections and mercury intrusion porosimetry. The methodologies for artificial ageing are as following: 1.) The samples were treated thermally by temperatures up to 600°C to induce various types of decay; 2.) All samples were additionally subjected to acid attack, freeze-thaw cycles and salt crystallization alone or in combination with thermal treatment. The approach of matching the ageing procedure for each lithotype to its predominant sensitivity and methods used to assess the effect of the ageing treatments are discussed in terms of relevance to the natural decay phenomena found in exterior environments of buildings. Thermal treatment proves to be a cost and time efficient method for assessing artificial ageing for testing of stone consolidants.

Keywords: artificial ageing, deterioration phenomena, consolidants, material testing

1. Introduction

Using sound stone to test the efficacy of consolidants in laboratory programs is likely to produce unrealistic results, due to the fact that these differ in their key properties from the weathered material. Unless a poorer quality of the same lithotype can be employed (Pápay and Török 2007, Ahmed 2015), ageing of the specimens prior to treatment is a prerequisite for such studies, though it must be kept in mind that artificial ageing will hardly result in a perfect mimic of true weathering states. While surface defects which could eventually be produced through salt or frost cycles causing, e.g. scaling or sanding, could in principle reflect true states of weathering usually associated with in-depth gradients, they don't

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match the needs of modern test standards, most of which base on the assumption of properties evenly distributed over the full diameter of the test body, e.g. a cube of 5×5×5 cm³. Lubelli *et al.* (2015) designed a method where the stones were ground and sieved to a grain size approximate to that of the fresh stone with the particles then re-aggregated on top of the fresh stone by the addition of air lime. While this method seems appropriate to study prerequisites of consolidants and promises to create different decay profiles going from granular disintegration to the sound fabric, it still needs further investigation in terms of physical and mechanical characteristics. The literature reveals some possibilities of ageing different lithotypes but most of them are time consuming, costly and bear negative side effects, e.g. salt contamination (Labus and Bochen 2012). Moreover most standards for determining the resistance of building materials by applying artificial ageing techniques (e.g. EN 12371:2010) focus on describing the failure of a material rather than achieving the level of degradation necessary to study consolidation products. It is generally accepted that salt as well as ice crystallisation causes major deterioration phenomena in building materials. Even though it is certain that damage will occur with Mg- and Na-sulphate solutions, it is first likely that decay processes induced by the action of salt are limited to the surface of the test body, and second it may be very difficult to desalinate the samples to the extent that a novel consolidants can be applied in order to study its fundamental principles. On the other hand, freeze-thaw weathering often causes premature damage in certain lithotypes while others remain unaffected. Systematic observation of fabric decay by frost action is not often considered after a material collapses or shows cracks going through samples. Ruedich *et al.* (2011) describes that in most cases at least 50 cycles need to be accomplished in order to investigate clear deterioration patterns. An important decay process induced by the action of water is described within clay-containing stones, which can be damaged through the swelling and shrinkage of clay by wetting and drying cycles (Jiménez-González *et al.* 2008). Generally, the observation of these deterioration mechanisms is rather slow and can be obtained only in long-term studies. Clay minerals can be treated with different acids, with the aim of partly dissolving them. Concentrated hydrochloric-, nitric- and sulphuric acid may dissolve clay minerals but due to their reactivity they preferentially dissolve carbonate binding materials by destroying their grain boundaries and consequently causing sanding and granular disintegration. Sulphuric acid and sulphur dioxide are used to form gypsum by reproducing a gradient of compactness within the specimen mimicking a crust on loose substratum (Janvier-Badosa *et al.* 2015). However, a negative side effect of using acids to age stone is the formation of salts, which hinders the ability to study innovative consolidants. Thermal ageing is a widely studied technique for fissure formation in compact stones. In particular, various marbles but also limestones have been studied in terms of their anisotropic behaviour and main factors that influence deterioration caused by thermal stresses (Siegesmund *et al.* 2000, Andriani *et al.* 2014). Researchers Sassoni and Franzoni (2014) have systematically studied weathering levels induced by heating prior to test consolidants. However, Franzoni *et al.* (2013) summarises that the process of heating may differ between the stones significantly and thus necessitating a development of suitable heating procedures for every lithotypes. Of these, the method that shows the best performance in terms of reproducing damage as found in-situ will be applied on a large number of specimens prior to test stone consolidants.

2. Lithotypes selected and their typical deterioration phenomena

Samplings of small specimens were taken to study typical decay phenomena occurring on three cathedrals, namely the Cologne Cathedral (Germany), the Cathedral in Pisa (Italy) and the Cathedral in Vienna (Austria). The tested lithotypes were two silicate based sandstones with a clayey matrix from Cologne and two carbonate based stones, a porous detrital limestone from Vienna and a marble from Pisa. Two basic types of defects can be observed and need to be reproduced: (1) granular disintegration is a characteristic feature of clastic sedimentary and some types of volcanic rocks as well as granular metamorphic rocks like marbles; and (2) fissuring of various kinds, characteristic of compact rocks such as dense limestones, siliceous metamorphic and plutonic rocks. In addition to the described defects, shales and crusts that tend to detach from the surface can be found in all lithotypes.

The main materials from the 19th century reconstruction used for the load bearing structure of Cologne Cathedral were quartz arenites named after the towns in which they were quarried: Obernkirchen and Schlaitdorf. Obernkirchen is a fine-grained quartz dominated sandstone. It is composed mainly of quartz and few lithic siliceous fragments with sutured grain contacts between quartz grains and with a slight authigenic growth of quartz. Additional occurrence of kaolinite and dolomite can be observed. Schlaitdorf quartz arenite is a coarse grained sandstone without a visible sedimentary layering. The main components are quartz and few lithic siliceous fragments. Furthermore dolomite (coarse grained spar cement and microcrystalline binder), kaolinite and illite are present. The Carrara marble from the Apuan Alps was used for the construction of the Cathedral of Pisa. It is a more or less non-foliated low metamorphic carbonatic rock mainly consisting of calcite and traces of dolomite. The last stone which was investigated is a fine- to coarse-grained, rhodolite bearing, neogene calcareous arenite from the quarry in St. Margarethen (Austria, Burgenland). In thin sections it appears very porous and is composed mainly of small fragments of coralline red algae and foraminifera. The components are cemented with fine-grained dog-tooth calcite cement.

3. Artificial ageing techniques and evaluation methods

General aim of all ageing tests was to widen existing pore spaces, loosen grain contacts, or create micro fissures to an extent that the stone fabric could still be classified compact enough to be handed for test reasons. A wide variety of techniques were employed either individually or in combination. The predominate methods for checking the efficacy of the ageing treatments was by determining the ultrasonic pulse velocity (apparatus Labek, oscillation frequency 40 kHz) and rate of water absorption by capillarity after one hour, which was tested after each heat cycle or acid attack. Ultrasound pulse velocity was measured after every 5th cycle of wetting and drying, freeze-thaw and/or salt crystallisation. Mercury intrusion porosimetry (Porosimeter Porotec Pascal 140/440) were measured on 3 samples when the desired state of degradation was achieved in comparison to the sound material. Polished thin sections were produced from the latter stone samples, which were then examined by polarizing light microscopy and scanning electron microscopy. For every ageing method three 5×5×2.5 cm samples were investigated.

The sandstones were heated up in a muffle oven to 600°C to form a sudden volume exchange through the conversion from α to ß quartz, which occurs at ~573°C. Thermal expansion is known to form anisotropic deformation of calcite crystals, therefore temperatures from 300 to 400°C followed by “quenching” in water of 20±5°C were used for marble. For the porous limestone higher temperatures were applied, from 400 to 600°C, to generate more stress and thus form micro cracks. The number of one-hour cycles used depended on whether the sample failed or had reached a “meta-stable” state; usually occurring between 3 and 5 cycles. The sandstones were additionally subjected to 80 wet/dry cycles (12 h water immersion by 20±5°C followed by 12 h drying at 75°C) as well as a 5% hydrochloride acid attack for partly dissolving the clayey matrix (12 h immersed and repeated 3 times). All lithotypes were aged by 25 cycles of freeze/thaw (12 h immersion in water by 20±5°C and 12 h freezing at -20°C). Another technique involved a two hour saturation of stones with a 14 % solutions of either magnesium or sodium sulphate, with a subsequent 16h drying out cycle at 75°C, which was repeated up to 25 times. With sodium sulphate, the specimens were dried at 100°C with addition of 350 ml water in the drying oven. Moreover the calcareous limestone was subjected to a 15 % sulphuric acid attack by a relative humidity of 50±5 %. The specimen was immersed edge-first into a 15 % sulphuric acid solution in order to draw the acid into its pore space till the top side is saturated. After ~24 hours of capillary absorption the side surfaces were sealed and the samples were put into water for one week so that a controlled evaporation only from the top side ensues. Nitric acid was additionally used for the limestone as it seems promising for stones with high porosity (Franzoni and Sassoni 2012). The samples were immersed in a 1.6 % solution for 24 h and afterwards washed for 3 days in an ultrasonic bath with constant change of the water. This ageing technique was repeated 3 times. A subsequent weathering effect was studied by immersing all samples into a 30 % hydrogen peroxide for the duration of 6 h and repeated 5 times. Finally the combination of heat treatment with freeze-thaw, hydrogen peroxide and acid attack was attempted, with the goal of forming susceptible damage.

4. Results and discussion

One concrete, reproducible result that could be attained quickly with thermal ageing was a reduction in ultrasound pulse velocity and an increase of water absorption capillarity, both of which correspond with a reduction in a stone sample’s soundness by formation of new micro cracks and the opening of existing cracks. A general finding was that heating the stone is by far the most time efficient way for any lithotype to deteriorate and to reach a reduction of strength (Tab. 1 and Fig. 1). A suitable temperature to cause the desired effects for Carrara marble is 400°C while other lithotypes show the highest decrease in soundness at 600°C. Care in heating and cooling the samples must be taken as macro-cracking can occur, such as in the case of Obernkirchen which can crack after the first heat cycle unrelated to its original texture. Thermal conductivity of stones and resulting stresses formed through rapid or slow cooling play a crucial role in the failure of samples. The overall results of thermal treatment may vary drastically if specimens with different size and shape are subjected to the same conditions of thermal ageing.

Tab. 1: Mean values of water absorption by capillarity after 5 cycles of heat treatment

Difference	**Carrara**	**Obernkirch.**	**Schlaitd.**	**St. Marga.**	**Units**
Sound	0.058	2.641	3.031	10.846	$kg/(m^2h^{0.5})$
Aged	0.854	4.235	5.337	12.074	$kg/(m^2h^{0.5})$
Increase	1364.29	60.37	76.08	11.33	%

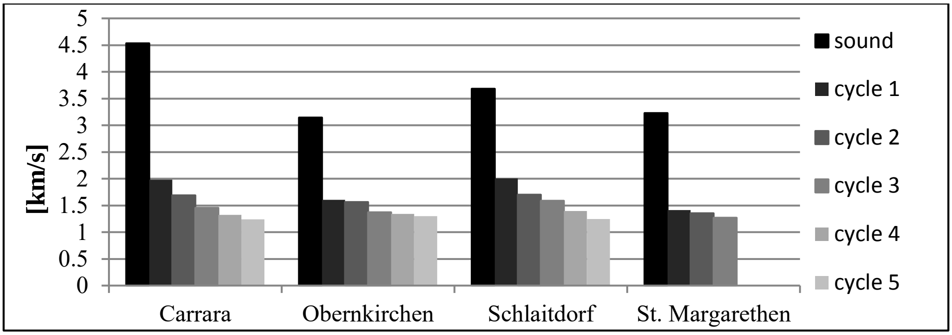

Fig. 1: Mean value of ultrasound pulse velocity after 5 cycles of heat treatment.

Following the measurement of water absorption by capillarity, the lowest increase can be seen in St. Margarethen limestone due to the high porosity of the stone that allows the calcite crystals more room for expansion without creating additional cracks. In this case, the rate of water uptake was constant after the 3rd cycle. As for the sandstones and the marble the relative increase of the capillary absorption is much higher due to the formation of inter- and intra-granular fractures, for example Obernkirchen shows an increase in water absorption after 3 cycles of approximately 25 % depending on its anisotropic orientation.

The evaluation of an aged stone's soundness by ultrasound pulse velocity shows the most significant drop after the first heat cycle but in the case of marble and the two silicates the velocity continues to decrease after additional cycles (Fig. 1). A stable state occurs after the 5th cycle. For St. Margarethen and very often also for Obernkirchen only 3 cycles are necessary to reach the lowest possible values. For the latter 3 cycles are likely to cause the failure of the sample. While some of the results may seem unrealistically low, for the testing of stone consolidants the lowest values should be taken even though in real life this condition indicates the danger of breakdown and the stones would either be replaced or put in a controlled environment (Siegesmund and Dürrast 2014). The highest possible deviation between sound and aged specimens make it possible to describe more accurately the difference of mechanical and physical properties of the stones and the performance of the consolidant.

The reasons for decay can be observed by scanning electron microscopy. The fissures created can be compared to the ones found in-situ (Fig. 2). The only difference is that the artificially induced cracks range through the whole specimens and are quite homogenous while the naturally developed occur only in exposed surfaces. While inter- and intra-granular fractures can be observed in the whole specimen, the natural decay phenomena show cracks parallel to the surface and thus contour scaling of different depths. Moreover the naturally decayed specimens show hollow spaces in a range of 10 µm up to 1 mm and the same effect can be achieved through thermal treatment. These effects are created due to the reduction of kaolin cement, some of which has been converted to meta-kaolin and re-deposited away from the grain boundaries and the formation of fissures within the silica grains (Fig. 2). On St. Margarethen calcareous arenite it is observable that the first heating results in the increase in porosity while re-heating the stone shows only minimal changes. This is due to the formation of micro-cracks that can accommodate more calcite crystals deformation and therefore a less significant drop is observed after this cycle, a phenomenon observed also by Sassoni and Franzoni (2014). It was observed that stones with smaller crystals size tend to crack faster during thermal ageing and depending on the shape large cracks and complete failures can ensue.

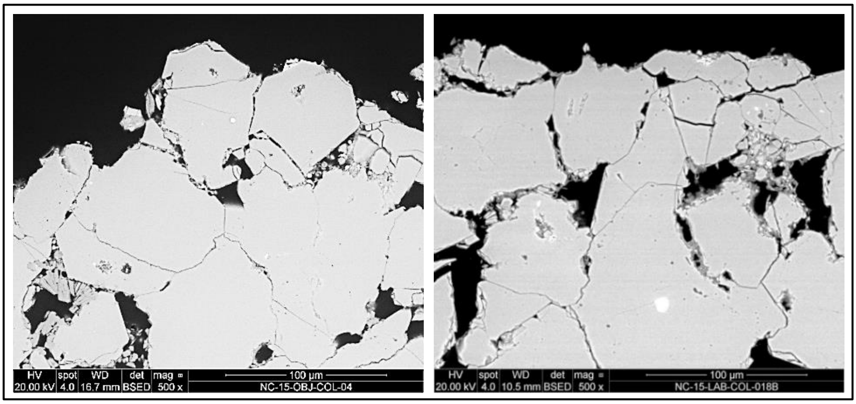

Fig. 2: Naturally (left) - compared to artificially aged (right) Obernkirchen Sandstone.

Tab. 2: Range of porometric parameters before and after thermal treatment.

	Carrara	**Obernkirchen**	**Schlaitdorf**	**St. Margarethen**
Total pore volume mm^3/g	2.79-3.90	74.77-79.79	62.26-72.96	119.02-130.90
	11.96-19.97	95.57-102.13	64.25-77.18	143.03-144.46
Total porosity Vol.%	0.76-1.05	16.66-17.29	14.65-16.11	23.65-26.17
	3.25-5.23	20.09-22.09	14.41-17.70	27.69-28.16
Average pore diameter µm	0.07-0.37	0.69-1.10	0.82-0.83	0.37-0.44
	0.53-2.38	0.59-0.67	0.25-1.09	0.42-0.54
Median pore diameter µm	0.20-3.28	6.14-6.28	20.88-29.96	48.92-49.81
	3.96-6.75	6.14-6.65	15.20-27.94	45.24-46.55

The changes in the pore structure can be determined by mercury intrusion porosimetry for all lithotypes. All lithotypes, in particular Carrara and Obernkirchen, show an apparent increase in total porosity. In the case of Carrara and Schlaitdorf this is accompanied by a shift in pore diameter, which should be investigated further through microscopy. However, the MIP results for St. Margarethen are of limited utility due to the heterogeneity of this lithotype.

The non-thermal ageing procedures gave very mixed results, which pointed to their marginal usefulness for the purposes of this study. However if the goal is the creation of surface or gradated phenomena to be evaluated by non-normative methods such as microscopy, a number of the following procedures may produce interesting results.

Hydrochloric acid was found to have the effect of reducing the soundness of sandstones when used in combination with heat-treatment due to a partial dissolution of the clayey matrix. Due to the formation of salt and the efficacy of the thermal treatment as a solely ageing method, ageing by hydrochloric acid will be omitted from future testing. In response to sodium sulphate crystallization only Obernkirchen fine-grained sandstone produced granular disintegration, sanding and flaking, which occurred as soon as after the 5th cycle. A rougher surface and light sanding could be observed on Schlaitdorf as well, while other lithotypes showed no damage that could be observed macroscopically. Magnesium sulphate showed no visible damage to any of the sample lithotypes after 25 cycles. With both sulphate solutions the evaluation methods did not show any significant difference despite the desalination. This, coupled with the difficulty of removing the salts before consolidation has led to the decision that this procedure be excluded from the future test program, but is of interest for additional research. The freeze-thaw ageing caused total failure of St. Margarethen limestone after as few as 3 cycles while other lithotypes remained sound after 25 cycles. Due to the complete failure of St. Margarethen and the different life cycles of the stones this method was aborted. Drying and wetting didn't cause any measurable changes after 80 cycles except colour changes due to the iron-containing components. While a gypsum crust was formed on the St. Margarethen limestone following partial immersion in weak acid, it was found to have a consolidating rather than degrading effect, at least in the short term. Since naturally weathered samples of all lithotypes show the formation of gypsum inside the fabric, the consolidation efficiency on a gypsum-contaminated substrate will be topic for further investigation. No significant changes could be observed with the ageing with nitric acid after 3 cycles.

Combining the above methods did not show a significant change in the degradation process. Thus even with a wide variety of treatments it was determined that thermal ageing is by far the most time efficient technique with reliably reproducible results.

5. Conclusion and Outlook

The degree of degradation is of major importance when studying stone consolidants; thus a systematic approach to age the substrate is required. Heat treatment allows a cost and time efficient reduction of soundness reflective of the degradation processes observed in-situ. Moreover the decay level can be specifically tailored and a systematic investigation of the efficacy is possible for every lithotype. Therefore the large scale production of samples on which to test consolidants will be mainly achieved through thermal treatments. Nevertheless, the results may vary drastically if specimens with different size are subjected to the same conditions of thermal ageing. Laboratory observations alone cannot always provide insight into understanding these interacting phenomena, but used in combination with numerical modelling these phenomena can be understood with greater precision, with the caveat that even these data are only roughly comparable with what occurs naturally. The influences of gypsum, salt and biological colonisation will be studied separately in advanced stage of this project. The most important conclusion of our research is that a set of standards for the artificial ageing of stone by lithotype is desirable.

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