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

EFFECT OF SWELLING INHIBITORS AND SELF-RESTRAINT ON THE DURABILITY OF ETHYL SILICATES CONSOLIDANTS APPLIED TO CLAY-BEARING STONES

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Abstract

This paper presents the study of the role of a swelling inhibitor on the durability of a clay-bearing stone consolidated with an ethyl silicate. It is shown that when the samples are left to swell freely, the swelling inhibitor reduces the rate of weakening of the stone in cycles of wetting and drying.

In the case where samples are restrained during the wetting, there appears to be a further reduction of the weakening for samples treated with swelling inhibitor before consolidation. However, this is not the case for samples consolidated without prior application of swelling inhibitors. The latter results require further work and improvement of experimental protocols to shed light on the possible role of self-restraint on the durability of consolidated clay-bearing stones.

Keywords: clay-bearing stone, Villarlod molasse, swelling clay, ethyl silicate, swelling inhibitor

1. Introduction

The preservation of stone-built cultural heritage is a challenge in material and conservation sciences. Many types of stones contain inclusions of clay minerals that may cause serious damage by dilatation during wetting and drying cycles, depending on the type, amount and distribution of the clay.

The application of ethyl silicates consolidants can be used as a treatment to strengthen weathered stone, by allowing the formation of silica gel network that acts as a binder within the stone. However, in the case of swelling stones, these consolidants can lose their effectiveness after just a few cycles of wetting and drying (Felix 1994). A remedy to the damage is to use these in combination with swelling inhibition products (Wendler *et al.* 1991). Positive synergies have recently been demonstrated (Jiménez González 2008), which restore particular interest for *in situ* application for non-transportable monuments and facades.

Furthermore, it is known that protruding elements get more damaged than facade ones in cycles of wetting and drying. This has been explained by the partial saturation of stone blocks, leading to partial expansion and lower stresses. This may also play an important role in increasing the durability of ethyl silicate consolidants with respect to laboratory tests performed on small and unrestrained samples. We examine whether the restraint felt by the consolidated part of the stones may also play such a role.

The aim of this research is to study the effects of a swelling inhibitor on the durability of an ethyl silicate consolidation treatment applied to a clay-bearing stone from the Swiss plateau. In this context we have further attempted to examine how "self-restraint" (occurring when the stone is not fully saturated with water) impacts this behaviour. The interest in examine the role of self-restraint lies in defining whether the damage in wetting and drying cycles of facade elements the loss of consolidation is really as critical as has been suggested up to now. These questions are investigated in terms of variations of ultrasonic velocities.

2. Experimental

2.1 Villarlod molasse

The Villarlod molasse is a subarkose sandstone, extracted in the Canton of Fribourg (Switzerland). It is available in two types: yellow and blue one. The blue variety was used in this study.

Under a geological point of view, the stones extracted in Villarlod are soft and porous sandstones featuring calcareous cement. About their stratigraphy, they are placed in the upper marine Molasse of the extra-alpine Tertiary (Burdigalian). The mineralogical composition of the stone is: quartz (50-60%), feldspars (10-15%), calcite (20-30%), glauconite (3-5%), biotite, mica blanc, epidote (minor quantities) and clays (2-10%). Around 30% of the clay fraction consists of swelling clays, mainly smectite or montmorillonite, ilite, chlorite and kaolinite. (Felix 1977; Jiménez González and Scherer 2004).

It is often used as a building material in Switzerland. Examples of its exploitation are the Cantonal and University Library of Fribourg, the Hotel de Ville and the Opera (formerly, Casino-Theatre) in Lausanne. (Felix 1977)

The stone was kindly supplied by Mr. Fred Girardet (Rino Sàrl, Blonay, Switzerland).

2.2 Consolidant and swelling inhibitor

The formulation Conservare OH (Tensid uk ltd, Addlestone, Surrey, UK) was used for consolidating the samples. Conservare OH is a solution of tetraethyl orthosilicate (30-60%), dibutyltin dilaurate (1-5%), butanone and acetone. Samples were consolidated by vacuum impregnation in a desiccator or by brushing the surfaces.

A 5% (w/w) aqueous solution of 1,3-diaminopropane dihydrochloride (98%, purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany) was used to limit the swelling of the stone.

2.3 Density

Bulk and matrix density measurements (Siegesmund and Dürrast 2011) were carried out on three ~50×50×50 mm^3 cubic samples, using a desiccator (to saturate the samples with water under vacuum) and a technical balance (PM1200) by Mettler-Toledo GmbH (Greifensee, Switzerland). The samples were previously dried in the oven at 105 °C for 16 h to remove any trace of moisture.

2.4 Sorptivity

Sorptivity measurements were carried out on non-consolidated and consolidated samples. The set up for this experiment is based on four PM4000 Mettler-Toledo technical balances interfaced with a serial connection to a Windows PC. The used software for data acquisition is a LabVIEW program (by Ernst Bleiker, ETH Zurich, Switzerland).

2.5 Wetting and drying cycles

Wetting and drying cycles were carried out in two different ways. In a first series of seven cycles, the samples were left to expand freely. The samples were either untreated, consolidated or first treated with a swelling inhibitor and then consolidated. Three samples were measured for each case.

After the seventh cycle, we examined whether restraint during wetting would alter the rate of loss of consolidation. For this two of the three samples from each of the consolidated group were wetted under load. This load was initially of 0.2 MPa, but was increased to maintain the position once the samples were wetted. For the wetting under load, experiments follow a protocol for swelling pressure measurements (Jiménez González and Scherer 2004; Jiménez-González *et al.* 2008). The third sample of each group was wetted without restraint.

In the first series of cycles samples were dried at 110°C, while in the second series of cycles they were dried at 105 °C.

Samples were cylinders with a core-drilled hole in their centre. Their dimensions were: outer diameter of about 45 mm, inner diameter of about 19 mm and height ranging from 36 to 48 mm. The bedding of the stone was chosen to be perpendicular to the axis of the obtained annular cylinders.

The instrument used for maintaining the samples under load was a 502/4000/100 testing machine by Walter+Bai AG (Löhningen, Switzerland). The used load capacity range was up to 20 kN and the load cell was a FL25UM(C)-2SGKT by Strainsert (West Conshohocken, PA, USA). The software for data acquisition was Proteus by Walter+Bai AG.

The used setup for wetting the sample while under load was custom made and its parts are shown in Figure 1.

Figure 1. The parts of the setup used for maintaining wet and under the load applied by the testing machine the core-drilled stone samples. From right to left, two drilled discs in polyoxomethylene to be placed on the top and on the bottom of the sample. The holes allow the water to get easily

into the samples; a core-drilled sample; the sealed container with the basis in stainless steel (not visible) used to contain the discs and the sample.

The position (and not the load) was kept constant by the instrument to simulate the restraining action of the dry bulk part of a protruding element (constituted by swelling clay-bearing stone) on the outer wet layer (see Figure 2), during an external wetting phenomenon.

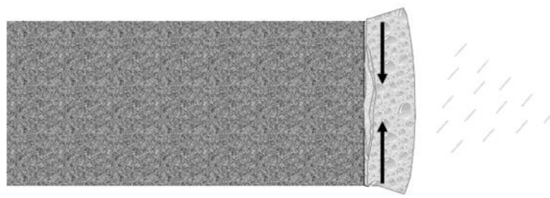

Figure 2. The compressive force arising when a block of clay-bearing stone gets wet does not necessarily lead to damage but the shear forces at the interface can cause buckling which has been observed on site (Jiménez González 2008; Jiménez González and Scherer 2004; Wangler et al. 2011). Adapted from Jiménez González (2008).

2.6 Ultrasonic velocity measurements

Ultrasonic velocity measurements were carried out on the above-mentioned core-drilled samples. The ultrasound velocity was measured in attenuation mode with a BPV ultrasonic tester by Steinkamp (Dr. Georg Steinkamp, Bremen, Germany) by applying a pulse at 50 kHz. The force applied on the samples was kept as constant as possible thanks to a spring mounted on the rail where the conic transmitter and receiver probes were placed. All the measurements were performed in a climate room at 20 °C and 65% RH. Before every measurement, the instrument was calibrated with a hard plastic reference block. Four measurements were taken on every core-drilled sample after every wetting and drying cycle.

3. Results and Discussion

3.1 Density

The obtained average bulk density is 2.22(4) g/mL, the matrix density is 2.59(5) g/mL and the porosity is 14.5(4)%. These values are similar (although more precise) to the ones reported in literature by Jiménez González (2008): 2.3 g/mL, 2.7 g/mL and 15%, respectively.

3.2 Sorptivity

The obtained average water absorption coefficient (*w*-value) for the untreated samples of Villarlod molasse is 6.1(5) × 10^{-3} g cm^{-2} $s^{-0.5}$. This is in the same order of magnitude of the one obtained by manipulating previously reported sorptivity data (Velo-Simpson 2004) with our porosity value and assuming the density of the water being exactly 1 g cm^{-3}: 4.5(6) × 10^{-3} g cm^{-2} $s^{-0.5}$.

20 days after the vacuum impregnation, the *w*-value of the same sample decreased to 0.41 × 10^{-3} g cm^{-2} $s^{-0.5}$. 62 days after the vacuum impregnation, the *w*-value increased

to 1.4 × 10^{-3} g cm^{-2} $s^{-0.5}$. This agrees with the corresponding criterion for successful stone consolidation (Snethlage and Sterflinger 2011).

These latter results suggest that the hydrophobic characteristics of the consolidated samples fade away in a couple of months, probably because a completion of the hydrolysis and condensation reactions. It is still an open question if, over a sufficient amount of time, such *w*-value would increase up to the value obtained before the consolidation treatment.

3.3 Ultrasonic velocity measurements

Results showing the evolution of the dynamic modulus of all samples measured in wetting and drying cycles are shown in Figure 3.

In the first series of cycles (up to the seventh one), the samples could swell freely. There it can be seen that there is a loss of modulus that is present for all samples whether they were treated or not. It confirms that clay-bearing stones undergo damage, even without any applied load and just because of the cyclic swelling and shrinking (Wendler *et al.* 1996). This modulus loss of the untreated stone is seen well in the right part of Figure 3, where the values are relative to the starting modulus. Interestingly, the loss of modulus of the untreated stone at the end of seven cycles lies in between the two series of consolidated samples.

In absolute terms, we can note that the consolidated samples remain substantially stiffer than the untreated stone despite their weakening during these cycles. This relatively good performance may be due to the vacuum impregnation procedure we used.

What is however more important in terms of consolidation of these stones, is to examine the role of swelling inhibitors. Again, in Figure 3, it can be seen that the swelling inhibitor reduces the stone weakening both in absolute and in relative terms. This confirms results previously reported by other authors for other stones (Wendler *et al.* 1996; Jiménez González 2008).

After cycle seven, we proceeded to examine whether restraint during load might modify the loss of consolidation. Here results are not very clear. We can observe that the modulus continues to decrease whether load is applied or not and whether swelling treatments were used or not. The question is to determine whether there is a difference in the rate of these changes.

From our limited set of data, it appears that for the sample without swelling inhibitor, the application of restraint does not play a role. For the samples with swelling inhibitor, results suggest that the application of load might limit the modulus reduction. However, results after such three cycles do not show a very important difference.

It is possible that having only exerted restraint during the wetting and not during the drying might have allowed samples to expand after the load was released and before the samples were allowed to dry. This is a clear shortcoming of these experiments and something that we have undertaken to resolve.

We should also point out that the drying conditions might be too drastic for the consolidant and unrepresentative of real site exposure Therefore, we are also planning additional experiments to define safe and representative drying conditions to be used throughout a new set of experiments.

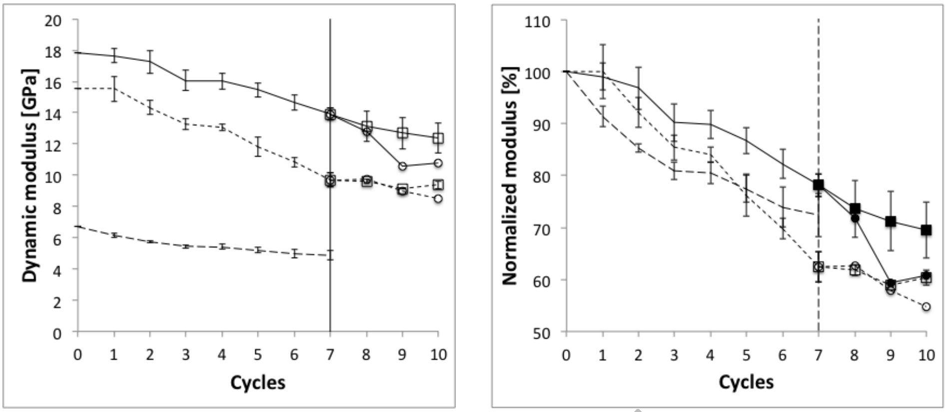

Figure 3. Evolution of the dynamic modulus. The bottom discontinuous line represents untreated samples. The intermediate dotted line represents samples consolidated with ethyl silicates. The continuous lines represent samples that were treated with a swelling inhibitor and then consolidated. The first seven cycles were performed without any load being applied. Samples were dried at 110 °C. After cycle seven, square symbols indicate samples wetted under restraint and circles are for the sample wetted without restraint. The vertical line at cycle seven just reminds that the way in which the wetting and drying cycles were performed had changed. Left: absolute values. Right: Relative values (with respect to initial modulus of each series).

4. Conclusions

The effect of swelling inhibitors on the durability of a clay-bearing stone from the Swiss plateau consolidated with Conservare OH ethyl silicate has been examined. It was shown that wetting and drying cycles alter the stone whether untreated, consolidated, or consolidated after treatment by swelling inhibitors. These changes are similar in relative terms, but, for the consolidated samples, there is nevertheless a significantly lower reduction if the swelling inhibitor is present. This confirms the relevance of applying such products before the consolidation treatment of clay-bearing stones with ethyl silicates.

Further experiments aimed at defining the role of self-restraint during swelling do not show clear effects. These experiments are only preliminary and require further work as well as improvements to the experimental protocol. They nevertheless suggest that self-restraint might further improve the longevity of samples treated both with swelling inhibitors and consolidants. In short, self-restraint does not seem to compensate for overlooking the benefits of swelling inhibitors. However, it might be "an added bonus" if such products are used. Further work is however needed to resolve these issues.

Acknowledgements

The help of Jan Bisschop from Institute for Building Materials, D-BAUG, ETH Zürich is kindly acknowledged for the mechanical characterisation.

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