EVALUATING THE POTENTIAL DAMAGE TO STONES FROM WETTING AND DRYING CYCLES

Inmaculada Jiménez González [1] and George W. Scherer [2]

[1] *University of Granada, Spain;* [2]*Princeton University, Dept of Civil & Env. Eng/ Princeton Materials Institute, Eng. Quad. E-319, Princeton, NJ 08544 USA*

Abstract: The literature on stone conservation often mentions that clay-containing stones can be damaged over time through cycles of wetting and drying (Félix 1988). Several studies demonstrate the deleterious action of these cycles on stones consolidated with ethyl silicates [Félix and Furlan (1994), Félix (1995)]. However, to our knowledge, only one study (Wendler et al. 1996) demonstrates that these cycles can damage unconsolidated stone. The procedure is rather long and probably this is the reason for which so little work has been done to examine the importance of this damage mechanism.

In this paper, we present a testing machine that has been developed to automate and accelerate the rate at which stone samples may be submitted to these cycles. Direct measurement of swelling indicates that swelling increases with the number of cycles, indicating progressive damage. However, the swelling can be durably reduced, although not completely eliminated by swelling inhibitors.

We use a novel technique to examine the behavior of swelling stones, which consists in measuring the warping of a thin stone plate placed on two supports and which is wetted from above. Deflection and relaxation of the plate can be analyzed to extract free swelling, the ratio of wet to dry modulus and the sorptivity of the stone. However, agreement with separate measurements requires introducing a separate kinetic expression for the rate of swelling.

Key words: sandstone; swelling clays; consolidation; wetting and drying; swelling; sorptivity; warping; swelling inhibitors, fatigue, elastic modulus

1 INTRODUCTION

Alteration of clay-bearing stones is often attributed to stresses arising from cycles of swelling and shrinking of the clays. However, to the best of the authors' knowledge, apart from stones consolidated with ethyl silicates [Félix and Furlan (1994), Félix (1994, 1995)], only one study successfully demonstrates this [Wendler et al. (1996)].

The experiments of Wendler et al. clearly establish that wetting and drying cycles can damage clay-bearing stones. Furthermore, they demonstrate that swelling inhibitors may actively reduce this damage, although they do not eliminate it completely. In previous work we have presented analysis of the stress development during wetting and drying cycles, showing to a first approximation that stresses should increase with free swelling strain, but that those could be significantly reduced by stress relaxation, the values of which were characterized by bending techniques (Jiménez González and Scherer 2004). Based on these results, in this paper we examine the main effect of this damage mechanism by determining the evolution of free swelling during cycles of wetting and drying, as well as the effect of swelling inhibitors during such cycles.

In addition, we use the warping technique (Scherer and Jiménez González 2005) to examine the variation of sorptivity and the ratio of the wet to dry modulus during these tests.

2 MATERIALS AND METHODS

Portland Brownstone, a coarse ferruginous sandstone quarried in the Connecticut River valley and widely used in the North East of America, was obtained from Pasvalco Co. (Closter, NJ, USA). This stone has been reported to suffer extensive degradation due to swelling clays. It is mostly composed of quartz grains coated by iron oxide films with a variable amount of feldspar and mica (flakes of muscovite), with a cementing phase mostly made of silica and clays. It shows evident bedding planes and samples discussed in this paper were cut so that water ingress would take place in the direction parallel to the bedding planes

By swelling inhibitors, we refer to products that limit or eliminate the swelling that clay-bearing stones undergo when exposed to water or humidity. We have shown that best results are obtained when such products are formulated as a mixture of various small organic compounds (Jiménez González & Scherer 2004). The mixture used in this paper involves a 1,3 Diaminopropane dihydrochloride ($H_2N(CH_2)3NH_2$. 2HCl) the use of which was first suggested by Snethlage and Wendler (1991) and a corrosion inhibitor for concrete based on aminoalcohols. The stones were treated by partially submerging them in a solution after having been oven dried. Further details are available elsewhere (Jiménez González & Scherer 2004). After this treatment the samples remain hydrophilic.

A home-made dilatometer was used to measure the linear expansion of the samples (Jiménez González & Scherer 2004). Samples were plates of about 100×22×3.6 mm with the bedding perpendicular to their longest dimension. The oven-dried samples (60˚C) were placed on end in a stainless steel sample holder. They were held in place by four plastic screws, which were found to stabilize the samples without preventing their swelling. The sample and sample holder were placed in a glass container and the pushrod of an LVDT was lowered on top of the sample to allow displacement measurement. After data acquisition was started, deionized water was poured around the sample until it reached the upper surface of the sample. As soon as the surface gets wet, the sample starts swelling.

Sorptivity measurements were performed with an electronic balance with a 0.001 g resolution and connected to a computer for a data acquisition (Scherer and Jiménez González 2005). A dish of water was raised into contact with the bottom of the sample and the weight change was continuously monitored.

To test fatigue resistance to wetting and drying cycles, as well as the duration of the swelling inhibition treatments, we built a special machine that can submit stone samples to a large number of cycles. This was necessary, because the initial manual testing with up to about 20 cycles did not show any significant change in mechanical properties of the stones.

The machine is illustrated in Figure 1. It consists of two parallel belts on which rings of stainless steel springs allow to fix up to 70 thin stone plates. Rotation of the wheels on which the belts are fixed brings the samples successively into a water bath and into a zone in which fans dry the sample. The duration of the cycles can be easily adjusted. However, in our experiments, the machine was set up so that the impregnation lasted 30 minutes and drying lasted 60 minutes, for the case of Portland Brownstone. The water bath has a large volume and a constant flow of water to avoid any contamination of the untreated samples by possible washout of the swelling inhibitors from the treated samples.

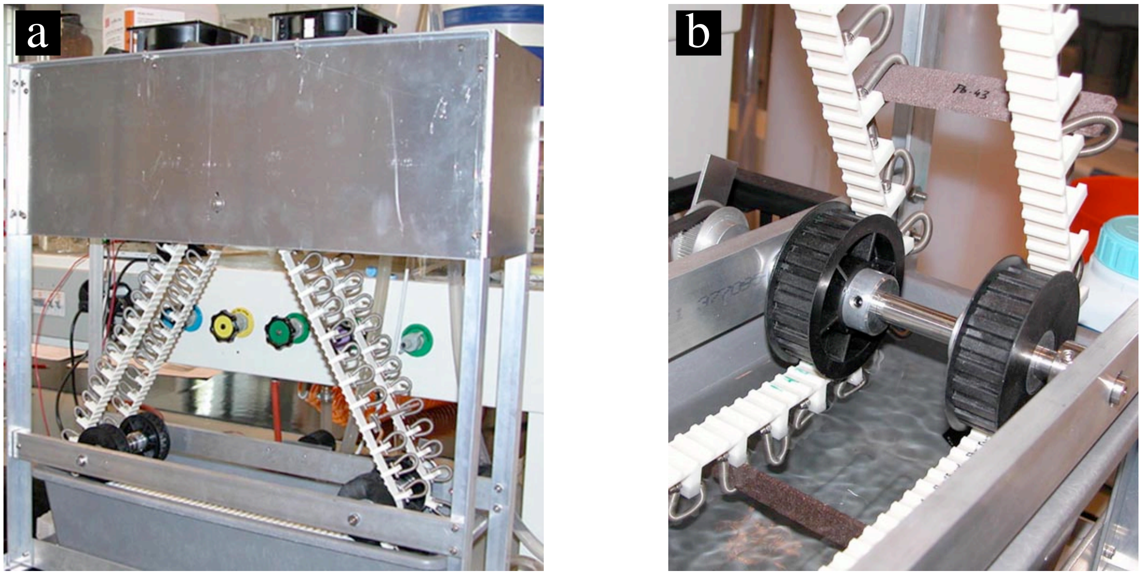

Figure 1. Wetting and drying testing machine. General view (a), detail of the bath and sample holder (b)

Details for the warping technique, which we have introduce for characterizing stones, can be found elsewhere (Scherer and Jiménez González 2005). In short, it consists in measuring the deflection of a thin plate of stone placed horizontally on two supports. The plate warps upwards as a result of adding water on its upper surface, and this is measured by a LVDT. A mathematical analysis described later gives the swelling strain, sorptivity and ratio of wet to dry modulus from the time dependent deflection of the sample.

3 RESULTS

3.1 Swelling

Results of the evolution of the free swelling strain obtained by direct measurement are reported in Figure 2. The samples Pb-22, 23 and 20 all received a treatment with the swelling inhibition mixture. The samples Pb-7 and 43 were not treated. The data indicate that this treatment reduces the initial swelling of this stone by about 42%. The data collected after 100, 200, and 700 cycles of wetting and drying show overall a gradual increase of swelling with the number of cycles regardless of whether they have been treated or not.

This increased swelling can be attributed to damage, in that a decrease of the material's stiffness will lower its ability to resist the swelling pressure caused by the wetting of the clays. From the perspective of conservation practice however, the important information of these results is that the effect of the treatment maintains the swelling of these samples well below their initial value, even after 700 cycles. Consequently, the treatment we propose reduces durably, but not indefinitely, the expansion and the associated damage. The aging of the treated samples may be due to the residual swelling strains or to a partial washout of the applied products.

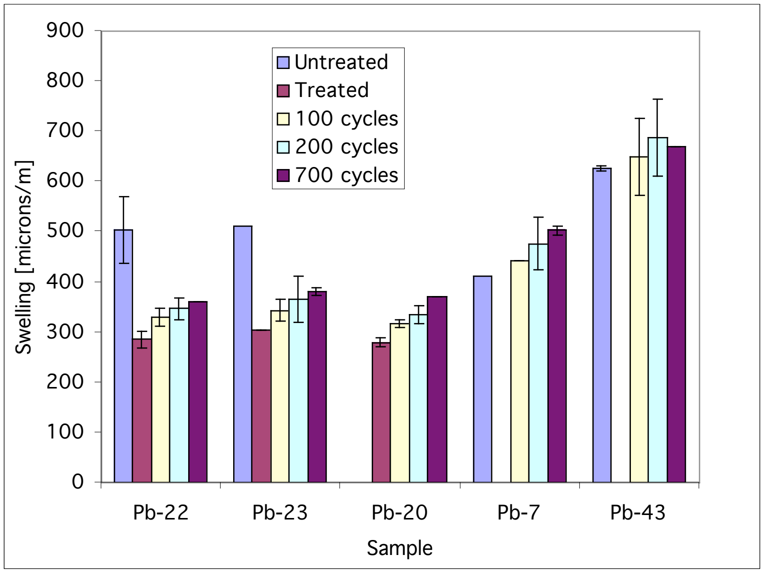

Figure 2. Evolution of the free swelling strain (direct measure) during the cycling

3.2 Warping

3.2.1 Swelling strain

In addition to doing direct measurements of swelling during these tests, we have also performed warping measurements on the same samples. The analysis of the warping experiment leads to the following expression for the height of the deflection, Δ, as a function of the depth to which the water has penetrated:

$$\Delta = \left(\frac{3w^2\varepsilon_{fw}}{4h}\right)\left(\frac{r(1-d)d}{d^4(1-r)^2-4d^3(1-r)+6d^2(1-r)-4d(1-r)+1}\right) \quad (1)$$

where w is the span of the plate, ε_{fw} is the free swelling strain, h is the plate thickness, d is the depth of penetration normalized by h, and $r = E_{wet}/E_{dry}$ is the ratio of the wet to the dry modulus.

The maximum of this curve is given by:

$$\Delta_{\max} = \left(\frac{3w^2\varepsilon_{fw}}{16h}\right) \quad (2)$$

Thus, in principle the height of the maximum deflection should be a direct measure of the free swelling strain. In fact, we find that although this measurement of the free swelling is correlated to the direct measurements discussed earlier, there is not a one-to-one relation, as can be seen in Figure 3.

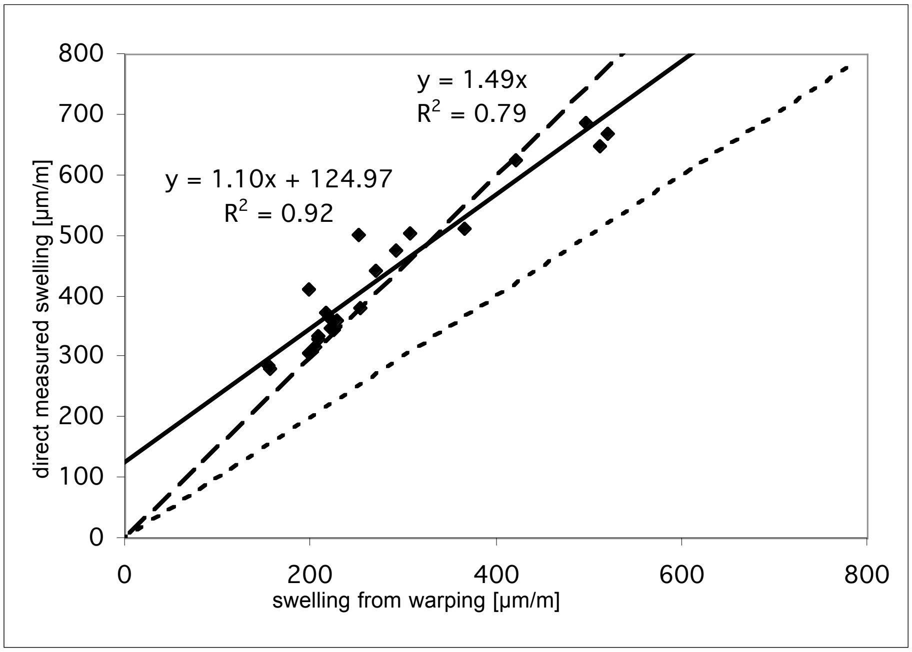

Figure 3. Relation between the free swelling strain obtained by the direct measurement and the warping measurement.

Indeed, we find that direct measurements of swelling strains are on average about 50% higher than those obtained from the warping measurement (dashed line). In fact, there is a better correlation if we admit the existence of an offset in the warping measurement. In that case the linear relation between both measurements is close to unity (solid line). Possible causes for this offset are discussed later in the paper.

3.2.2 Sorptivity and modulus ratio

Equation (1) can also be used to estimate the sorptivity and the ratio of wet to dry modulus. For this we write the rate of water ingress as:

$$d = \frac{S}{h}\sqrt{t} \tag{3}$$

where S is the sorptivity and t is the time.

It can be shown that the initial slope, a_0, of deflection versus $\sqrt{t}$ is equal to

$$a_0 \equiv \frac{d\,\Delta}{d\sqrt{t}} = \left(\frac{3\,w^2\varepsilon_{fw}}{4h}\right)\frac{r\,S}{h} = \frac{4\,\Delta_0\,r\,S}{h} \tag{4}$$

The time needed to reach the maximum deflection is:

$$t_{\Delta\max} = \left(\frac{h}{S\sqrt{1+r}}\right)^2 \tag{5}$$

Thus equations (4) and (5) can be used with the measured values of the initial slope and time to maximum deflection to obtain the ratio between wet and dry modulus, *r*, and the sorptivity *S*.

It turns out here again that there is a discrepancy between the values estimated by the warping measurement and direct measurements; however, in this case the direct measurements were performed on different samples than the warping tests, owing to experimental requirements. The values of *r* are in the range of 0.35 for direct measurement, while they are estimated at about 0.6 by warping. Direct measurement of sorptivity is in the range of 0.01 $cm/s^{1/2}$, while values from warping are about 0.025 $cm/s^{1/2}$. Possible reasons for this are discussed below.

4 □□□ DISCUSSION

4.1 Warping measurements

We have found, contrary to our preliminary experiments with this technique (Scherer and Jiménez González 2005), that there is a discrepancy between the three parameters estimated from warping measurements with respect to independent measurements of the same parameters. In the particular case of the swelling strain the situation cannot be attributed to sample-to-sample difference, because the same samples were used for both measurements. These discrepancies reveal the complexity of the kinetics of expansion, so they deserve careful study.

To analyze the possible origin of these discrepancies, we now focus our attention only on the samples measured before treatment or cycling. One way of doing this is to see whether there are dependencies among the different parameters.

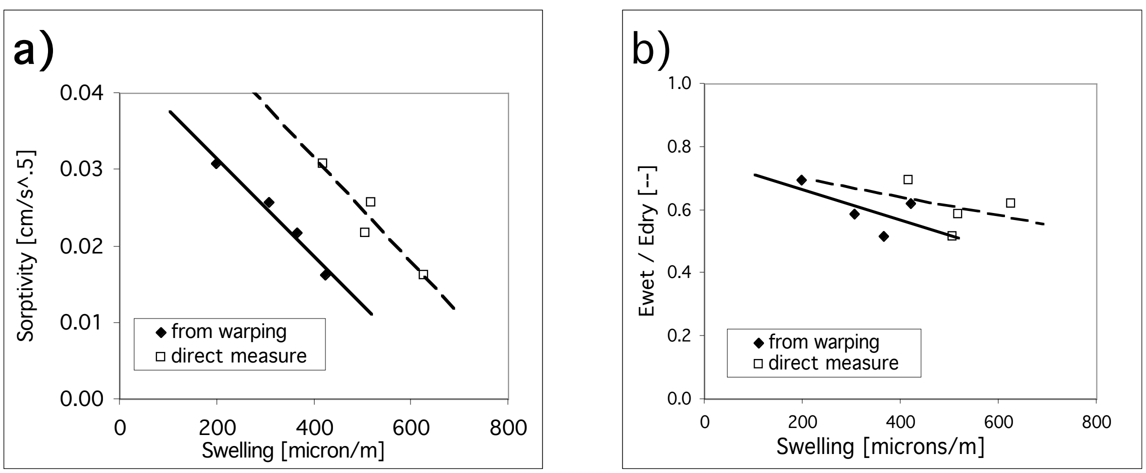

Figure 4. Dependence of sorptiviy (a) and modulus ratio, r (b) on the swelling strain. Values are plotted with respect to both the direct swelling strain measurement and the one inferred from warping

From the data in Figure 4, we can see that sorptivity clearly decreases when the swelling strain increases, while the modulus ratio is relatively unaffected by it.

Sorptivity experiments show that there is an initial stage of faster water ingress. This complicates the analysis of the water experiments by requiring the introduction of a kinetic expression for the changes in sorptivity and for the rate of expansion, which are not necessarily linked in a trivial way one to the other. Finally, there is also the possibility that the softening of the wet stone is time dependent which would also account for the discrepancy in ratios of wet and dry modulus.

As the simplest approach, we will assume first that the kinetics of sorptivity change are the same as those of swelling. We have found that sorptivity curves could be well fitted in the following way:

$$d = \left(\frac{\Delta_S \alpha \sqrt{t}}{1 + \alpha \sqrt{t}} + S\sqrt{t} \right) \frac{1}{h} \tag{6}$$

where Δ_S is the intercept of the linear regression to the sorptivity curve, when plotted as height of rise versus square root of time, and $\Delta_S \alpha$ is the difference between the sorptivity at time zero and the one at steady state.

Using, an average value of 0.13 cm/s$^{1/2}$ for the sorptivity at steady state, values from independent measurements of swelling strain and modulus ratio, we fit the initial part of the curve by adjusting the values of Δ_S and α. The agreement is good, but clearly insufficient at longer times (Figure 5).

At this stage our treatment for the delayed expansion just multiplies the swelling strain of the wet part by the hyperbolic part of the equation (6): $\alpha\sqrt{t}/\left(1+\alpha\sqrt{t}\right)$. Any further adjustment that improves the fit to the deflection after the maximum spoils the fit at short times.

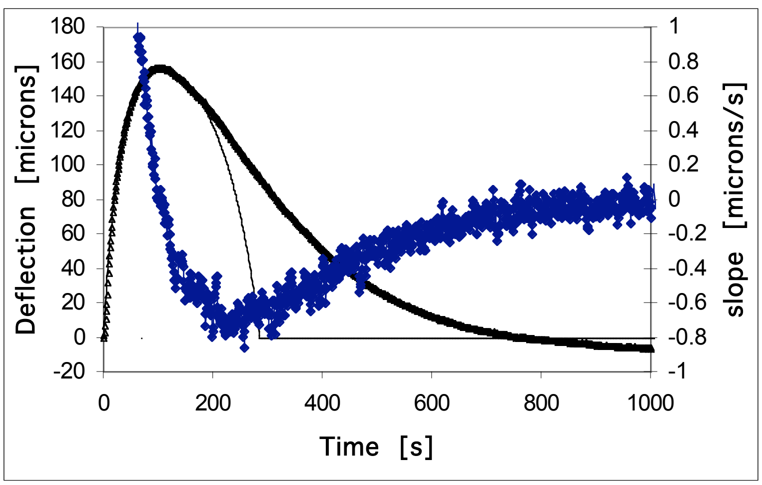

Figure 5. Comparison of a warping curve with the fitted function using the same time dependent function for sorptivity and swelling.

From the fitting parameters, we predict that the sample will be completely saturated at ~280 s. From the slope of deflection versus time (secondary axis in Figure 5), we determine a minimum at 230 s, which can reasonably be attributed to a change in deflection mechanism when the water reaches the other side of the sample. The similarity of these estimates supports the validity of the fitting parameters we obtained.

Recent results by Wangler (2005) suggest that other factors, including evaporative cooling of the liquid pool on the sample, and capillary pressure from the pore liquid, may contribute to the post-peak deflection. Studies are underway to quantify those effects.

5 CONCLUSIONS

We have examined the durability of a clay bearing stone exposed to accelerated cycles of wetting and drying. From direct measurements of swelling it appears that samples either treated or not with a swelling inhibitor, show an increased expansion over time. However, even after 700 cycles the swelling of the treated samples remains significantly under values before the application of the product, which indicates that this treatment has a durable effect in reducing damage from wetting and drying cycles which increases with the extent of swelling.

In addition we have examined in more detail the warping test by performing swelling and warping tests on the same samples. Both tests show the same trends but differ quantitatively as do values for sorptivity and modulus ratio. Agreement can be improved if the warping test is analyzed by introducing a time dependent change of sorptivity and swelling based on similar kinetics. The pertinence of the fitting parameters is strengthened by the fact that they provide a satisfactory estimate of the time the water takes to cross the sample in this test. Additional work is needed to describe the rest of the curve, taking account of other phenomena that contribute to deformation of the sample.

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