CONTROLLING STRESS FROM SWELLING CLAY

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Abstract: Many sedimentary rocks contain clays that swell on exposure to moisture, producing stresses from differential strain. Wendler and Snethlage showed that the swelling can be reduced by treatment with α–ω diamino alkanes. In this paper, we present results showing that mixtures of such molecules are more effective than any single molecule, and that better results are obtained by applying smaller molecules before the larger ones.

Key words: clay, swelling pressure, stress, fracture, surfactant, intercalation

1. INTRODUCTION

Many sedimentary rocks contain clays that cause swelling when the stone is exposed to moisture[1], resulting in damage to the civil infrastructure[2] as well as to monuments and works of art[3,4]. Expansion of clays results from the presence of alkali ions between the charged layers in the crystal structure of the clay[5]. Water molecules are electrostatically attracted to those ions, so they penetrate between the layers and surround the alkali ions, resulting in expansion. The pressure needed to prevent invasion of a monolayer of water molecules can be hundreds of MPa in bentonite, but this drops drastically as additional layers of water molecules accumulate[6]. The clays can form a layer surrounding grains in the stone[7], so their swelling is directly reflected in expansion of the stone; moreover, the softening of the wet clay reduces the stiffness of the stone[8]. The damage is generally attributed to differential strain from expansion of the wet region of the stone, but the clay may also contribute to damage from salt[9] by creating small pores that are particularly susceptible to high crystallization pressure[10].

Wendler and Snethlage[11,12,13] demonstrated that the expansion of clays could be substantially reduced by treatment with α–ω diamino alkanes (hereafter called DAA), which are molecules having amine groups at each end of an alkane chain. Whereas similar molecules with a single amine group cause increased swelling, the α–ω structure allows the molecule to bond to adjacent sheets in the clay structure, binding them together. The charged sites on the clay layers are randomly distributed[14], so Jiménez González and Scherer[15] reasoned that no single molecular size would allow binding to all of those sites. They demonstrated that the swelling of Portland Brownstone was reduced more by a treatment with a mixture of surfactants than with any one alone. This observation was confirmed in a study of sandstones by Velo-Simpson[16]; in addition, she found that the order of treatment with the surfactants had some influence on the swelling. In this paper, we present results of a study using sequential or simultaneous treatment with DAA having alkane chain lengths ranging from 2 to 10 carbons. This provides a direct test of the importance of the size and dispersity in size, as well as the order of application, of the surfactant on the amount of reduction in swelling.

2. EXPERIMENTAL PROCEDURE

The surfactant treatments employ diaminoalkane molecules (Acros Organics) dissolved in water for easy application. The DAA has a linear carbon chain linking two amine end groups, with the general formula $H_2N\text{-}(CH_2)_n\text{-}NH_2$. The shorter chains (n = 2, 3, 4) are shipped as salts with hydrochloric acid forming the amine salts, or $HCl\text{-}H_2N\text{-}(CH_2)_n\text{-}NH_2\text{-}HCl$; the diaminohexane (n = 6) was not neutralized. The solubility of these molecules decreases as the carbon chain length increases, but is adequate to achieve concentrations of about 0.5 M for $n \leq 10$. To indicate the number (n) of carbons in the alkane chain, we will identify them as DAAn; thus, diaminopropane will be written as DAA3.

The stone used in this work (supplied by Dr. George Wheeler, Metropolitan Museum of Art, New York City) is a sandstone from Aztec Ruins National Monument in New Mexico (http://www.nps.gov/azru/).

Samples were cut on a diamond saw to approximate dimensions 3 x 3 x 12 mm. The expansion was measured using a differential mechanical analyzer (Perkin-Elmer DMA7). The DMA has a temperature control unit that is raised up around the sample; within that unit, the sample is separated from the heating coil by a nickel cup. The cup was filled with water, so that the sample was immersed when the unit was raised; temperature was maintained at 30˚C.

Surfactant treatments were applied by placing the stone sample on a layer of glass beads in a petri dish, then adding the solution to the dish until it just touched the bottom of the sample. The dish was hermetically sealed and left for two hours, during which the stone was saturated by capillary rise of the solution. The sample was then left in the hood for an hour and then placed in a convection oven at 60˚C overnight.

The elastic modulus of the stones was measured in three-point bending using apparatus described in detail elsewhere[15,17]. To obtain the static Young's modulus, the sample was driven up and down at a rate such that relaxation would be negligible; samples were run dry and while immersed in a water bath. To measure the kinetics of stress relaxation, a displacement was imposed suddenly (stabilized in ~0.5 s) and held constant for several hours while the force on the beam was monitored continuously. Samples used for these tests were in the form of rectangular plates with dimensions of 2-3 x 5-10 x 50 mm, and were immersed in water during the test.

3. RESULTS

The untreated stone showed an expansion of 1.33×10^{-3} in water, which is about three times as large as the swelling of Portland Brownstone[15]. The effect of treatment with DAA is summarized in Table 1; sample-to-sample variations were about 10-15%. All of the surfactant treatments cause impressive changes in swelling, but some patterns emerge. A second treatment always helps, presumably because the stone is thereby exposed to more amine groups. For example, a single treatment with a mixture of DAA2 and DAA3 reduces the expansion by 73%, and a second treatment with the same solution provides a total reduction (compared to the untreated stone) of 83%. Multiple treatments with mixtures provide no advantage over sequential treatments with individual surfactants. For example, treating twice with a mixture of DAA2 and DAA6 gives about the same improvement (85%) as sequential treatments with DAA2 followed by DAA6 (84%). Again, these sequences expose the stone to the same total molarity of amine. This is not the whole story, though, because a 5% solution of DAA2 + DAA3 contains less amine than DAA2 + DAA6, but it causes a slightly greater reduction in swelling; therefore, the size of the molecule is significant. The best result was obtained with sequential treatment with DAA2, 3, 4, and 6 (91%). Of course, this quadruple treatment exposes the stone to more surfactant. What is most striking is that reversing the order of treatment substantially reduces the effectiveness of the treatment, even though the amount of exposure to amine is the same. This suggests that the order of addition can be important, perhaps because the smaller molecules open the interlayer space, so that it is more easily entered by the larger molecules. This may also explain why a second treatment with DAA2 + DAA6 makes such a great improvement: the first exposure to DAA2 may open the interlayer space so that both amines penetrate during the second treatment.

Table 1. Effect of treatment with diaminoalkanes

Treatment[a]	$M(NH_2)$[b]	Strain (%)[c]	% Reduction
None	0	0.1330	-
2+3	0.72	0.0356	73
2+3 / 2+3	0.72 / 0.72	0.0222	83
2 / 3	0.76 / 0.68	0.0198	85
3 / 2	0.68 / 0.76	0.0171	87
2+6	0.80	0.0490	63
2+6 / 2+6	0.80 / 0.80	0.0197	85
2 / 6	0.76 / 0.80	0.0209	84
4 / 6	0.62 / 0.80	0.0350	74
2+3+4+6	0.72	0.0252	81
2+3+4+6 / 2+3+4+6	0.72 / 0.72	0.0228	83
2 / 3 / 4 / 6	0.76 / 0.68 / 0.86 / 0.80	0.0119	91
6 / 4 / 3 / 2	0.80 / 0.86 / 0.68 / 0.76	0.0360	73

[a] Integer represents number (n) of carbons in alkane; plus (+) indicates components of mixture; slash (/) separates sequential treatments. [b] Molarity of amine groups in solution. [c] Strain measured when oven-dried sample immersed in deionized water.

The static elastic modulus of the stone dry or saturated with water is shown in Table 2. Young's modulus drops by about a factor of 4 when the stone is wet, owing to the softening of the clay. Treatment with the DAA mixture (2+3+4+6) raises the modulus by ~30% in the dry state and 100% in the wet state.

Table 2. Static Young's modulus, *E* (GPa)

Condition	Untreated	Treated
Dry	7.55	10.3
Wet	1.87	3.91

Damage to monuments from swelling of stone occurs during wetting, owing to buckling of the wetted surface[18]. The maximum stress, which occurs when the wetted layer is thin[15], is given by

$$\sigma_S = -\frac{E_{wet}\,\varepsilon_S}{1-\nu_{wet}} \qquad (1)$$

where ν_{wet} is Poisson's ratio for the wet stone, and can be estimated to be ~0.25. As shown in Table 3, treatment with DAA reduces the compressive stress by as much as 70-

80%, even though the static modulus is increased. Note that these stresses are all calculated using the modulus of the stone treated sequentially with DAA 2/3/4/6, which probably has a higher modulus than the other treated stones; consequently, the actual stress reduction may be greater than shown in the table.

Table 3. Effect of treatment on stress during swelling.

Treatment[a]	Stress (MPa)[b]	% Reduction
None	-3.3	-
2+3	-1.9	44
2+3 / 2+3	-1.2	65
2 / 3	-1.0	69
3 / 2	-0.89	73
2+6	-2.6	23
2+6 / 2+6	-1.0	69
2 / 6	-1.1	67
4 / 6	-1.8	45
2+3+4+6	-1.3	60
2+3+4+6 / 2+3+4+6	-1.2	64
2 / 3 / 4 / 6	-0.62	81
6 / 4 / 3 / 2	-1.9	43

[a] Integer represents number (n) of carbons in alkane; plus (+) indicates components of mixture; slash (/) separates sequential treatments. [b] Calculated from eq. (1) using the measured strain for each treatment and the elastic modulus (3.9 GPa) measured on the sample treated with once with 2/3/4/6.

The stress relaxation behavior of the wet stone, before and after treatment with the DAA mixture (2+3+4+6), is shown in Figure 1. As was observed previously[15], the treatment raises the elastic modulus, but accelerates the rate of relaxation, probably by a stick-slip mechanism. This effect further reduces the stresses resulting from swelling in treated stone.

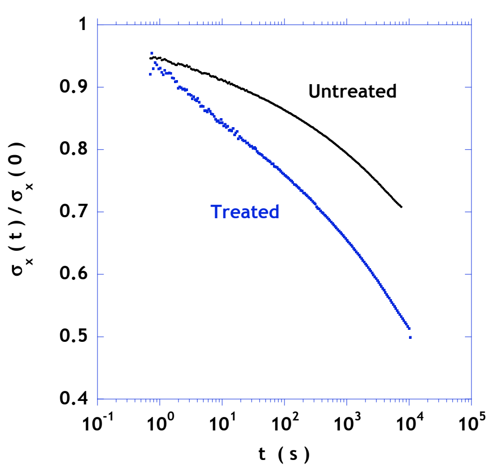

Figure 1. Stress relaxation of wet stones in three-point bending, before and after sequential treatment with DAA 2/3/4/6.

4. CONCLUSIONS

The use of a mixture of α–ω diamino alkanes with different molecular sizes offers significantly better performance than any single molecule. The treatment also changes the viscoelastic properties of the stone, increasing the stiffness. To reduce the stress caused by hygric swelling, the treatment must reduce the expansion more than it raises the modulus. This has proved to be the case in our experiments, so the treatments are expected to reduce damage caused by swelling of the stone.

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