

Chemical softening and hardening of geomaterials *in situ*

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ABSTRACT: Dependence of mechanical properties of geomaterials on the variable chemical environment or advancement of chemical or mineralogical reactions is known to be a crucial factor in many cases of mechanical stability of geo-masses. Processes of mineral dissolution usually results in material weakening while precipitation of minerals such as of silica in aging or calcite in clay fractures may lead to material strengthening. Experimental background of the process of aging of deep sediments is presented. It is postulated that aging consist of two processes of dissolution and precipitation affecting two different structural components. Their respective chemical softening and chemical hardening within plasticity theory is described. The joint response of the two components to further loading is then modeled.

1 INTRODUCTION

In many long-term engineering endeavors involving geomaterials, and whenever natural geological scale processes affect engineering works, engineers tend to resort to study creep, to take into account “time effect”. However, the very term “time effect” may appear in various circumstances to be an excessive shortcut. Instead, one may use, and in many cases there is a sufficient information for it, an intrinsic time, or a process, or reaction advancement measure, to follow the evolution of the mechanical behavior over long-term histories.

It what follows we will focus on one specific phenomenon related to the “time effect”, namely aging of petroleum/gas bearing sediments. This problem is socially important because of the serious consequences in terms of subsidence of the sediments that the exploitation of the resources may have on environment and on on-shore human habitat, in particular. Aging of soils is known as a set of processes of evolution of the mechanical properties of soils subjected to a long – term duration constant load (Schmertmann, 1991). Because of an impracticality of reconstructing the geological history of the sediments, on one hand,

and of the need to quantify the progress of aging with the testing of the current state, it is proposed to try to link specific chemical processes resulting in the observed mechanical property changes.

2 EXPERIMENTAL EVIDENCE

Materials used for testing were: a predominantly clayey sand: DALIA 1, and a clay (50% smectitic), TEA 1, coming respectively from the depth of 1210 m. and 3270m of the prospective natural gas recovery fields in Northern Adriatic Sea. The most significant test result is derived from the comparison of a monotonic, incremental loading oedometric test and what will be called “aging test”, which includes a monotonic loading to the stress equal to that *in situ*, followed by a pause at a constant loading of duration of 14 days, followed then by resumption of the monotonic loading. While it is realized that the “aging test” does not reproduce the loading history of the actual sediments exactly, in summarizes its essential aspects. The *in situ* effective stress was determined from stratigraphic data as 12.6 MPa for DALIA 1, and 35.04 MPa for TEA 1. Figure 1 shows two tests for comparison for DALIA 1. Surprising as it may

be, TEA 1 clay behavior presents very similar characteristics. The 14 days the aging episode resulted in a modest secondary compression strain. The stress-strain curves below the aging episode are nearly identical, but they diverge significantly after it, showing a visible stiffening of the material. It appears that the amount of the stiffening in sand and clay is comparable, despite the difference in terms of depth, amount of the *in situ* stress, void ratio, and the total amount of strain reached. From the engineering point of view, it is clearly the range of stress above the *in situ* stress that is of direct interest. Indeed, in the case of oil/gas extraction the decrease in pore pressure of the extracted fluid will induce a corresponding effective stress increase. For that reason the stress – strain curves portion above the *in situ* stress, or the post-aging behavior is focused on in what follows.

On the basis of the above results four principal characteristic aspects of the post-aging behavior of undisturbed material were identified, which are crucial for the subsidence prediction (as shown for TEA 1 in Figure 2). These are: (i) decrease in incremental compressibility moduli in the post-aging stress excess range; (ii) relative reduction in strain in the post-aging stress excess range; (iii) a stress excess range affected by (i), (iv) strain gain during the aging period. The first three characteristics affect directly the numerical prediction of subsidence, the fourth one may be a factor in the experimental determination of the three former ones. There is another important characteristics of the post-aging behavior, which is (v) the total post-aging stress excess or total strain reduction range, defined as the total range in which the stress is above the comparable stress, and the strain is below that in reference monotonic tests. However, the values were not measured in the performed tests, because they were much higher than expected, and resulted to be outside the test range.

The above characteristics (i) and (ii) of the post-aging behavior, both expressing the decrease in deformability have a different connotation. The decrease in the incremental moduli expresses a local effect, which is stress dependent. The strain reduction is an integrated effect and gives a global measure of the aging impact, over certain stress range above the aging stress level. The standardized stress excess value corresponds to the value at which the incremental moduli decrease

falls to zero. The stress range is defined as that in which the incremental compressibility moduli are lower than in the reference tests, as opposed to the total stress range (v) where the stress value is above that in monotonic stress.

To convey the sense of the effects of aging numerically, relative (normalized) values calculated for the three of the characteristics discussed above are summarized in Table 1, in terms of the average values below.

Table 1

material	relative reduction in rate uniaxial compressibility modulus, c_M	relative strain reduction due to aging	relative stress excess range affected by aging
DALIA	49.4%	38.0%	12.0%
TEA	69.9%	44.0%	45.0%

All relative changes are divided by the respective variables at the moment of the onset of aging.

Several other aging history effects were addressed in the experiments on remolded material. First, it appears that sediments have the memory of their previous aging episodes. Tests on remolded DALIA-1 B8 and B10 samples show that when aging is repeated at the same stress level after a cycle of a partial unloading, the amount of strain per unit time during the “second aging” is more than one order of magnitude lower than during the “first aging”. Secondly, the rate of straining changes significantly after 24 hours (‘switching’ from a pore pressure driven consolidation to secondary compression), but it is also clear that the rate of secondary compression does not decrease significantly after 14 days. However, stiffening of the material seems to occur much faster. Two accidental, short duration, aging episodes were investigated. An episode of a 2_ hour duration (Figure 3) in test B4 on DALIA-1 sand shows a significant decrease in deformability modulus (75%). However, the stress range affected by the short-term aging is relatively small, 6% of the aging stress level, against 28%, for a longer term aging. Finally, it was found that for longer (7 months) duration tests, the mean strain developed during aging was 0.759%, against 0.187% in 14-day aging (Figure 4). However, the decrease in compressibility modulus over 7- month is from $4.61 \times 10^{-4} \text{ cm}^2/\text{kg}$ to $1.935 \times 10^{-4} \text{ cm}^2/\text{kg}$, that is 57.9%, against analogous decrease for 14- day

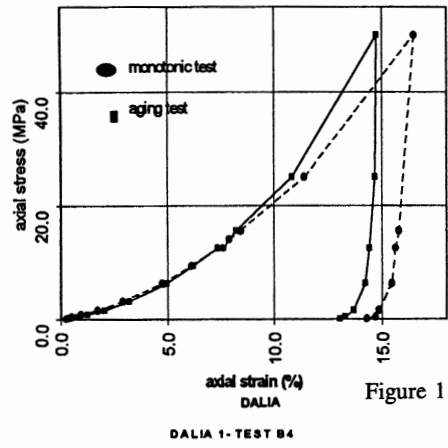


Figure 1

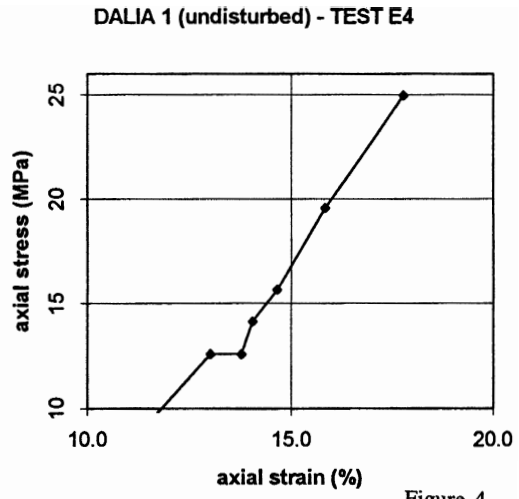


Figure 4

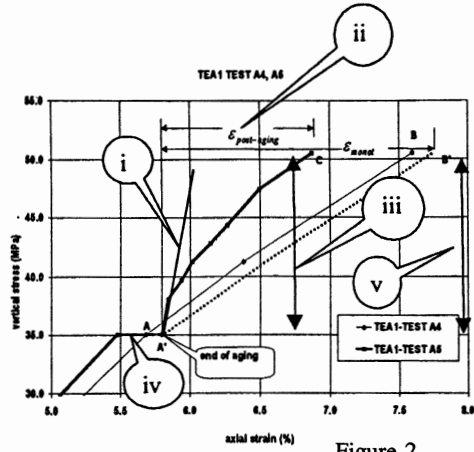


Figure 2

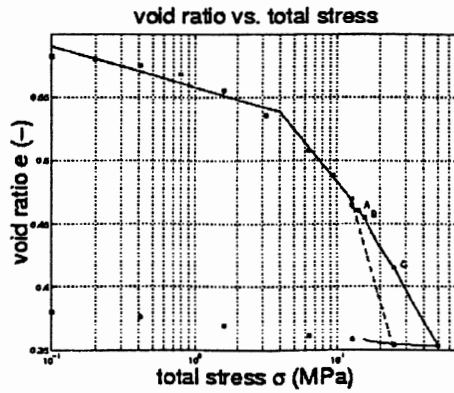


Figure 5a

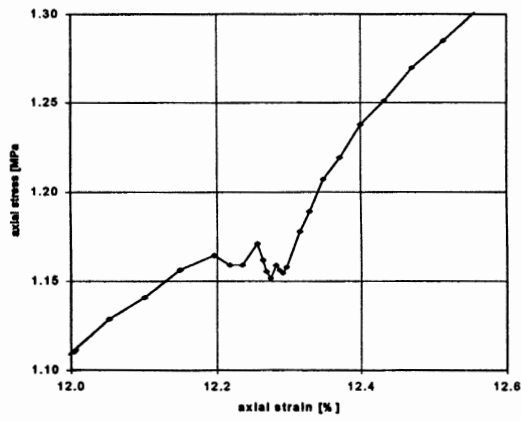


Figure 3

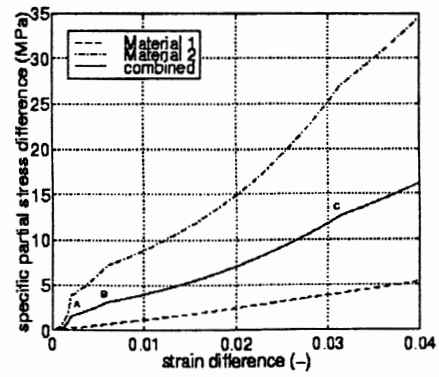


Figure 5b

tests of 52%, in average. This showed that some effects of aging such as strain amount, or stress range are more time dependent than others, and that decrease in compressibility is less dependent on the test duration than other effects.

3 SIMULATIONS OF AGING OF DALIA 1

The actual physico-chemical processes leading to the overall process of aging are far from being even sketchily known. Earlier hypotheses and some experiments (Mitchell and Solymer, 1984) suggested that dissolution of some minerals in the primary structure (silica in the case of sand, and montmorillonite in the case of clays), which is known to be facilitated by the inter-granular stress concentration, may contribute to an initial weakening and deformation of sediment. A subsequent change in electrolytic properties of the pore liquid (gel formation) are seen as contributing to building a secondary structure bonding by silica acid gel film particles of the primary structure through precipitation of silica from solution or suspension and acting as a cementing agent between them. Alternatively, the dissolution of the stressed solids at contact points into the pore liquid, may turn the liquid into a stress carrying suspension, flocculate or gel.

To endow such hypotheses with a quantitative framework, we shall use a two-component, evolving soil microstructure model for the aging conditions outlined by Hueckel et al., 1999. In this model an initial (primary) structure exists in an unloaded soil consisting of a system of grains. At the constant *in situ* stress linked to the overburden, dissolution of the stressed mineral at grain contacts of the primary structure may lead to its irreversible strain. Further during aging the dissolved silica (or other mineral dissolved) precipitates onto this primary structure forming a secondary structure. The partial stress components $\sigma^{(I)}$ and $\sigma^{(II)}$ are total stresses carried by the individual fractions, calculated per total area of the considered element, whereas $\sigma^{(1)}$ and $\sigma^{(2)}$ are specific partial stresses occurring in the material of each fraction, calculated per area of that fraction. Any additional compressive stress is distributed between the two components, because the two materials now deform jointly. Thus, a strain rate is a (weighed) sum of the rates of the partial stresses,

$$\dot{\sigma}_{ij} = \dot{\sigma}_{ij}^{(I)} + \dot{\sigma}_{ij}^{(II)} = \dot{\sigma}_{ij}^{(1)}\alpha + (1-\alpha)\dot{\sigma}_{ij}^{(2)} \quad (1)$$

In a simplest option coefficient α , $0 < \alpha < 1$ is related to the volume fraction of the material in the (constant) total volume of solids. It is assumed for simplicity that the secondary material remains unstressed and undeforming during aging, or that dissolution and precipitation processes are sequential.

The chemical process as we see it is composed of two chemical reactions: of dissolution of mass from the primary material with the rate ξ_d , followed by precipitation of the dissolved material with the rate ξ_p . The dissolution is assumed to mechanically weaken the primary material. The precipitation is assumed to strengthen the secondary material. These processes will be described in terms of chemical softening and chemical hardening plasticity, following Hueckel (1992). Yielding of each of the two materials occurs when a Cam – clay type yield function and its rate are zero for that material,

$$\begin{aligned} f^{(i)} &= (p^{(i)})^2 - p^{(i)} p_c^{(i)}(\varepsilon_v^{pl}, \xi^\alpha) + (q^{(i)} / M^{(i)})^2 = 0; \\ df^{(i)} &= 0 \end{aligned} \quad (2)$$

p' and q are the first and second deviatoric invariants of specific partial stresses of the two materials. $M^{(i)}$ are coefficients related to internal friction angle for each material. To describe the weakening and strengthening of the considered components, the apparent maximum past isotropic stress describing hardening $p_c^{(i)}$, is a function of the respective degrees of advancement of reactions defined through time integral of the reaction rates ξ_α , $\alpha = d, p$. They are also functions of usual volumetric plastic strain (joint).

$$p^\alpha = p_{c0}^\alpha \exp \left[\frac{(1+e_0)\varepsilon_v^{pl}}{(\lambda-\kappa)} + r^\alpha \varepsilon_v^a \xi_\alpha \right] \quad (3)$$

r^α is the coefficient of chemical softening or hardening, p_{c0}^α is the maximum past effective mean partial stress, and ε_v^a is the strain value at the onset of aging. Using relative values of stress and strains with respect to those at the onset of aging is a modification of the formula used by Hueckel et al.

(1999) to enable us to use the data from remolded specimens to simulate undisturbed material, based on previous findings. λ and κ are bulk moduli of Cam-clay model.

It is assumed that the material element is a closed system, i.e. that no mass is exchanged with the external environment during the reactions. Therefore, the reactions are governed by the kinetic rate equations of the dissolution or precipitation of the respective minerals. We furthermore propose that

$$\dot{\xi}_p = -\dot{\xi}_d \quad (4)$$

This means that the mass of primary material is dissolved at the same rate as it precipitates to form the secondary material.

Following Hueckel et al. (1999) we will exploit a postulate by Leroueil et al., (1996) and Peret (1995), that during aging there is an unusual growth (about 3 times higher) of shear wave velocity across the material and that this indicates structuration of the material. We shall thus use the change in initial shear modulus as a measure to quantify the precipitation reaction rate and indirectly to measure the development of the secondary material structure.

It is recognized that the processes in the primary and the secondary material are completely different also from the plasticity point of view. The primary material undergoes chemical softening compensated completely by the strain hardening needed to fulfill two conditions: that of yielding and of constant effective specific partial stress in the primary material, $df = 0$ and $d\sigma' = 0$. This leads to the possibility of measuring the rate of dissolution in terms of plastic strain rate,

$$\frac{d\xi_d}{d\varepsilon_v^{pl}} = - \left(\frac{\partial f}{\partial \xi_d} / \frac{\partial f}{\partial \varepsilon_v^{pl}} \right) \quad (5)$$

Knowing both the advancement of dissolution reaction and the plastic strain rate one may identify the chemical softening constant, r^d

$$dp^1 = dp_{c0}^1 = p^1 \left[\frac{1+e_0}{\lambda-\kappa} d\varepsilon_v^{pl} + r^d \varepsilon_v^a d\xi_d \right] = 0 \quad (6)$$

However, while dissolution rate is not known, an alternative is to use the hypothesis that $\dot{\xi}_p = -\dot{\xi}_d$. Furthermore, we shall assume a linear form of the Leroueil – Peret postulate change in the elastic shear modulus, G_0 , (initial modulus of

unloading, or “dynamic modulus”), with respect to that at the onset of the secondary compression G_0^a

$$\dot{\xi}_p = \dot{\xi}_0 \dot{G}_0 / G_0^a \quad (7)$$

Thus the coefficient of chemical softening can be found from (6) and (7) as

$$r_{\xi}^d = r^d \xi_0 = - \frac{1+e_0}{\lambda-\kappa} \frac{d\bar{\varepsilon}_v^{pl}}{d\bar{G}_0} \quad (8)$$

where $\bar{\varepsilon}_v^{pl} = \varepsilon_v^{pl} / \varepsilon_v^a$ and $\bar{G}_0 = G_0 / G_0^a$

if the rate of change of shear modulus and of the volumetric plastic strain is measured. It should be noted that since the primary partial stress is constant, so is the elastic strain, and that also the secondary partial stress is by definition equal to zero. The latter statement however does not imply that the secondary material is inert during aging and it undergoes a strain-less hardening due to the precipitation of minerals with the rate $\dot{\xi}_p$ at an elastic state. Thus,

$$dp_{c0}^2 / p_{c0}^a = r^p \varepsilon_v^a d\xi_p > 0 \quad (9)$$

Using again the Leroueil-Peret postulat, knowing from the experiment the aging induced total stress excess, and from the properties of the primary material being able to calculate the secondary partial stress difference (proportional to the yield surface size growth in the secondary material), we can deduce the precipitation hardening constant, r^p .

In the tests on DALIA 1 material, the changes in the velocity of the shear waves were measured for remolded specimens and at a (fictitious) aging stress of 0.808 MPa. Table 2 shows corresponding void ratio and calculated shear modulus variations.

Table 2

B5		B6	
void ratio	shear modulus G (MPa)	void ratio	shear modulus G (MPa)
0.6678	185.4	0.6797	205.2
0.6673	219.0	0.6794	218.7

The first row data refer to the aging onset. With the data contained in Table 2, the mean value of the two cases for dissolution softening constant r_{ξ}^d from

eq.(8) is obtained as equal to 0.678 with $\lambda = 0.0538$ and $\alpha = 0.0082$ for the primary material. For the secondary material, with the stress excess of 0.023 MPa, and the elastic material constants back-calculated $\kappa = 5.81$, with $\alpha = 0.629$. The precipitation hardening coefficient is obtained as $r_{\xi}^p = r^p \xi_0 = 5.81$. These coefficients, obtained from tests on remolded material will now be used for the simulations of the behavior of undisturbed specimens, under the premise that when properly normalized the behavior of both materials exhibits the same characteristic, at least in some processes.

The objective of this exercise is to evaluate the roles of the primary and secondary structure in the post-aging phase. The aging strain is taken directly from the experiments. The material parameters for the primary material were identified on the basis of the pre-aging phase behavior. The constants for the secondary material are back-calibrated. The chemical softening/hardening effect is based on the portion immediately preceding and two portions immediately after the aging episode.

The main result concerns the stress partition. Fig. 5a shows the results in terms of void ratio and logarithmic stress. Fig. 5b presents the re-calculated specific partial stress difference-strain difference relationship above the aging stress in the linear stress scale. The partial stress difference in the secondary material is clearly higher than the corresponding partial stress difference, above the aging stress in the primary material. However, the total partial stress in material (1) is the stress difference seen, plus its "initial" aging stress, that is 12.59 MPa, whereas in material (2) the initial stress is zero. Thus, the absolute partial stress in material (2) is lower than that in material (1) until the strain difference of 0.05 above the end of aging. The specific partial stress in primary material is larger than that in the secondary material up to the strain of about 0.03. Finally, the primary material is in the plastic state in the whole range above the aging stress. The secondary material reaches yielding at the value of 4.2 MPa of the specific partial stress, corresponding to the partial stress of 2.18 MPa and to the total stress of 14.77 MPa. Thus, even if in terms of stress differences material (2) carries more load than material (1), in terms of the absolute stress values, this is not the case. Actually, in terms of pre-consolidation stress, material (2), at the moment of

its yielding, carries less than $\frac{1}{2}$ of the specific partial stress that is carried by the primary material.

4 CONCLUSIONS

From the engineering point of view, it is the load above the *in situ* stress that is important. In carrying this load the role of the secondary material is more important than of the primary one. Consequently, also its yielding point is extremely important, because it defines what was earlier called as "stress excess" due to aging. Thus, understanding of its strength is crucial for the prediction of the stress range in which the decreased compressibility occurs.

5 ACKNOWLEDGEMENT

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