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EFFECT OF ANIONIC-DETERGENTS ON THE CONSOLIDATION OF CLAYEY SOILS

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Abstract

One of the major groups of anthropogenic contaminants entering the soil are detergents. Although due to their solubility in water, the process of soil remediation is perhaps a less complex problem than e.g., in the case of hydrocarbons, they can still remain in the soil and cause significant changes in the different properties of the soil. The aim of this series of measurements is to investigate the effect of the detergent as a pollutant on the consolidation of clayey soil. The results showed that contamination had a significant effect on soil consolidation. The one-way analysis of variance (ANOVA) on the resulted data confirmed that the difference between clean and contaminated sample is caused by the presence of detergent rather than a random factor influencing the data set.

Keywords: *clay, consolidation, detergent, oedometer, soil contamination*

1. Introduction

Soils form complex systems with different proportions of mineral, organic matter and fluid content. They are found in their natural state in an impurity-free form in the upper segment of the lithosphere. As a result of human activity (e.g., industrial, agricultural activities) pollutants of different composition may enter the soil (the phenomenon is called anthropogenic pollution in terminology). These contaminants can significantly endanger not only the soil system itself, but the surrounding biosphere (e.g., plants, water supplies, animals, humans). Soil pollution is most common in cities and industrial facilities. The latter is also a serious problem in Hungary, as there are many industrial areas in the country where serious soil contamination has occurred due to improper facility operation. The re-use of these areas can only be achieved through complex remediation (and financial) processes, but even after site remediation the natural state of the soil usually can't be achieved. Some amount of the pollutant remains in the soil (up to a regulatory threshold limit) or the total volume is left using MNA (monitored natural attenuation) as a remediation strategy. The 219/2004 (VII.21.) "Government Decree on the Protection of Groundwater" defines the limits of the remediation target state (D): "the concentration prescribed in the official decision, which must be reached as a result of the remediation, will affect human health, the ecosystem and the environment in order to prevent damage to elements."

During the remediation works and the determination of the target value, the goal is often to reach an acceptable value, which does not necessarily correspond to the original state of the environment. On the one hand, this may be due to the specifics of the area and pollutant, the selection of the most effective remediation method and, last but not least, the question of ensuring cost-effectiveness. The area-specific acceptable value determined in this way can be multiple times the pollution limit value (B) also determined by this government decree. It is also a widespread method, during which the remediation process is actually a natural decrease in the concentration of the contamination (this can occur during destructive processes such as: dilution, dispersion). Of course, this procedure can only be used if the given contamination does not pose an environmental risk.

Due to the presence of anthropogenic contaminants, the chemical, physical and biological properties of soils may change. These changes can be observed in many properties, be it the organic matter in it or even the soil's hydraulic conductivity. The aim of the present study is to understand the changes in the geotechnical properties of clay soils, with an emphasis on the changes in the consolidation parameters due to various contaminations.

2. Important soil characteristics of clayey soils

First, it is necessary to distinguish between the concepts of clay and clay mineral. While the first is a fine-grained raw material, it is a lithological definition used for residual weathering, hydrothermally modified, or sedimentary deposits. Furthermore, clay, a term that also appears during grain distribution studies, is used to name the smallest particle fraction (according to the current upper limit, - which is also used in Hungary -, it is 0,063 microns). Clay minerals can be divided into the following groups according to their composition and structure: kaolinite, smectite, palygorskite–sepiolite, illite, chlorite, and mixed-layered clays. In addition to the mineral composition, there are several non-mineral constituents in clay minerals that can significantly affect their properties. These can be, for example, organic substances, exchangeable ions or even soluble salts. (Murray, 2007)

2.1. Clay minerals

Clay minerals are a group of materials with many unique properties: their layer structure (in one dimension) is in the nanometer range, the thickness of a 1:1 (TO) structure (typical of clay minerals) is about 0.7 nm, and the thickness of a 2:1 (TOT) structure is 1 nm.

Furthermore, an anisotropic arrangement of the layers as well as the particles is observed. They are also characterized by high plasticity and hardening due to temperature changes (drying or firing). It is also important to highlight the unique properties of the 2:1 layer structure, which are: the particles are colloidal in size; they have a large specific surface area; high number of exchangeable anions (which is less dependent on the pH of the environment); moderate charge between layers; interlayer swelling is observed under the influence of water.

A few words are worth mentioning about the surface properties of clays, as they significantly influence their behavior with contaminations. The properties of the outer surface of clay minerals are mainly determined by the chemical composition, the nature of the atoms on the surface (oxygen and hydrogen), the type and extent of surface defects, and the charge of the layer and the type of exchangeable cations.

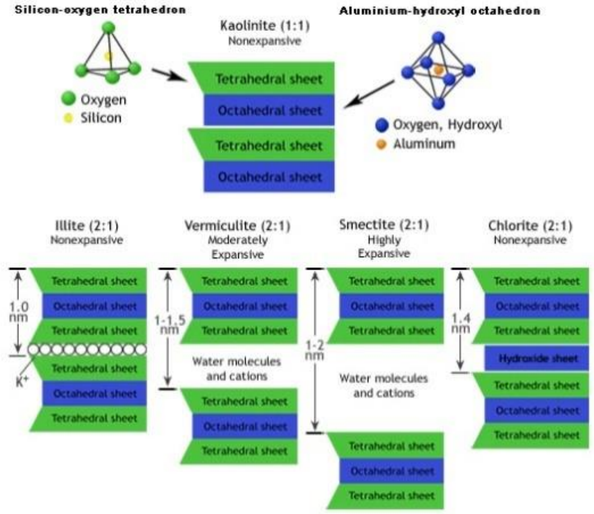


Figure 1. *Structure of clay minerals (Lory, 2015)*

2.2. Diffuse-double layer

The interfacial properties of clay particles, as they significantly influence the behavior of clay soils against contaminants. The properties of the outer surface of clay minerals are mainly determined by the chemical composition, the nature of the atoms on the surface of the particle (oxygen and hydrogen), the type and extent of surface defects, and the charge of the layer and the type of exchangeable cations. An influential factor to highlight is the so-called 'diffuse double layer' interface phenomenon, which develops at the boundary between clay particles and fluids. Due to their particle size, clays can be classified as colloids, forming a continuous transition between the solid (micellar core) and the liquid phase (dispersed layer) on the surface of colloidal micelles (Stefanovits et al., 1999) This boundary layer has different properties than the liquid and solid phases and plays an important role in the ion exchange and adsorption processes at the interfaces. Moving away from the colloidal particles, the concentration of adsorbable cations decreases while the anion concentration increases. From this it can be concluded that the cations closer to the surface of the particle bind to the surface with a stronger bond, forming a more ordered layer (Stern layer). The more distant layers are more disordered, forming a diffuse layer. On the surface of the colloidal particle is a layer of highly directed water molecules, with cations on the outside that make up the Stern layer. As a result, a potential difference is formed on the surface of the soil solution and the particle, which decreases exponentially as it moves away from this interface and becomes equivalent to 0 upon reaching the outer boundary of the solvate layer. This type of distribution is called a diffuse-double-layer.

The thickness of the double diffuse layer fundamentally influences the behavior of the clays. The thickness of a diffuse double layer depends on a number of factors and conditions.

In geotechnical practice, it can be used to understand and estimate the expected behavior of soils against contaminants. (Szabó et al., 2019)

The resulting soil structure is the result of a combination of several factors, which depends on the lattice structure of the clay mineral, surface charge, ion exchange, adsorption, on the other hand it depends on its composition, concentration, charge of the ions present, permittivity, temperature, and even external conditions (e.g., load).

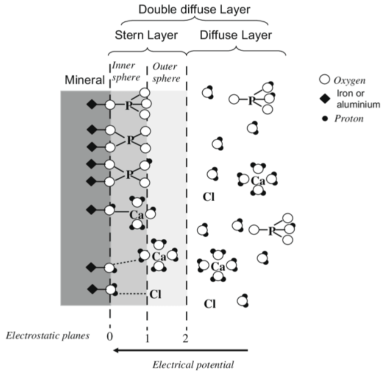


Figure 2. *The thickness of the double diffuse layer (which is a function of several factors) significantly influences the behavior of a given soil. In order to understand the behavior of clays in geotechnical practice, we must take this factor into account. (Devau, 2009)*

3. Consolidation of soils

Soil consolidation is a reduction process by which a fully saturated, low water permeability soil sample undergoes a gradual decrease in volume under effective stress. One reason for this may be the pore water located in the pores between the soil particles and the drainage of this pore water. The process continues until the excess pore water pressure due to the increase in total stress is completely dissipated. Consolidation can also occur due to a decrease in the pressure of the pore water, e.g., from groundwater pumping or well extraction. The simplest case is one-dimensional consolidation, when the stress increase is applied in only one direction (usually vertically), and the value of the lateral displacement is 0. It is worth mentioning the phenomenon often occurring in the case of clay soils, the process of swelling, which can be considered as the inverse of consolidation. A gradual increase in the volume of the soil can be observed with a negative excess of pore water.

The compaction caused by consolidation means vertical displacement of the soil, and during the process a change in volume can also be observed. This type of compaction can be caused by facilities built on clay soil (which put extra stress on a given layer) or even if the groundwater level above the clay layer is permanently reduced. Consolidation can also be observed in cases where there is a significant lateral stress in the soil assemblage, in which case even the deformation of the soil contributes to the consolidation of the soil. Soil consolidation is an in-situ phenomenon that can be traced by using piezometers (Craig, 2012)

3.1. Study of soil consolidation under laboratory conditions

During one-dimensional consolidation or swelling of soils, the variable parameters can be characterized under laboratory conditions using a test device called an oedometer.

A disc-shaped soil sample is used for the test, which is inserted between the confining rings. These rings provide the lateral frame of the specimen, preventing it from moving horizontally (the inside of the rings is designed to minimize lateral friction). At the bottom and top of the soil sample is a 1-1 filter stone (or geotextile suitable for the purpose) that prevents soil leaching. The compression due to the load is recorded by a displacement sensor on the load cap. The load is gradually applied to the specimen, the load being maintained until the growth period ceases (excess pore water pressure is completely dissipated, and the total stress applied is equal to the actual vertical stress.).

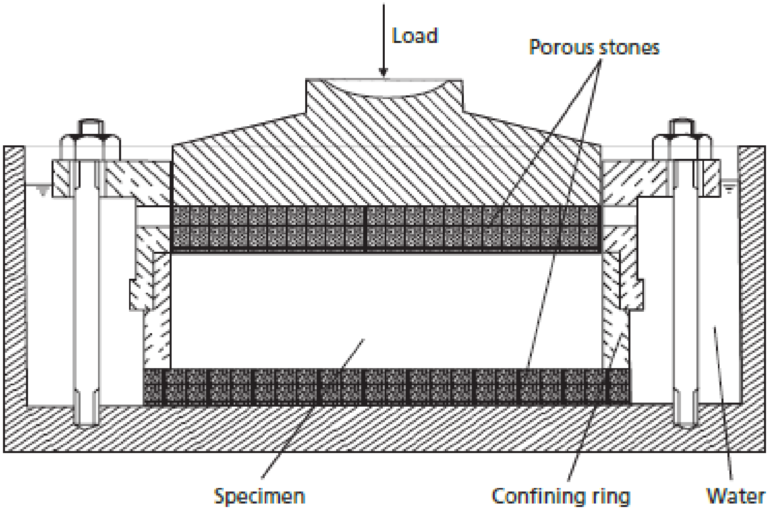


Figure 3. *The oedometer apparatus (Craig, 2012)*

The displacement sensor, which measures the changes in the load, is transmitted to the computer, where the software of the instrument displays them in “real-time” as a function of the elapsed time.

“Gray clay” from a clay mine near Mályi (HUN) was used for the investigations. The name was later clarified, based on consistency as well as grain distribution studies, and was defined as a lean clayey silt. The soil has a low organic matter content and a water absorption capacity of around 50-53%, which is a typical value of muddy soils. The test series were performed as described in the previous section, on 3 clean and 3 contaminated samples.

The model material used as a contaminant was an anionic detergent (50 w/w% concentration). According to the basic concept of the study, the degree of consolidation in the soil samples changes due to the presence of the detergent substance. The soil sample was stored in hermetically sealed storage boxes for 1 month after manual contamination. This one month (based on previous research and literature articles) was an important period because during this time, chemical reactions between the soil particles and the contaminant could occur or even level off.

3.2. Test results for non-contaminated samples

During the measurement, the load was applied gradually and evenly, for a total value of 800 kN/m^2.

For the interpretation of the results compression curves were used. From this curve, the compressibility modulus of the soil, which is the stress associated with a unit specific compression, can be interpreted. From the measured vertical deformation (ΔH) and the original height (H) of the specimen, the specific deformation (ε_z) can be determined:

$$\varepsilon_z = \frac{\Delta H}{H} * 100; \quad (1)$$

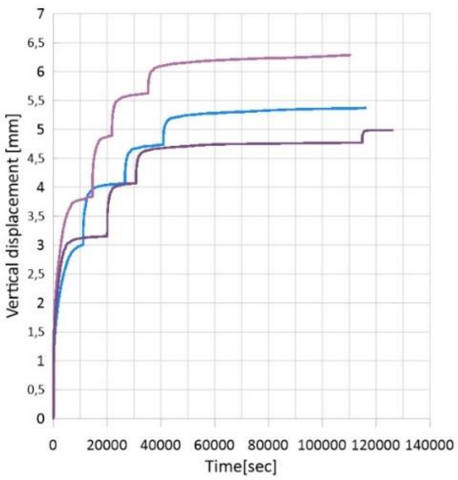


Figure 4. *Representation of vertical deformation as a function of time elapsed in clean soil samples.*

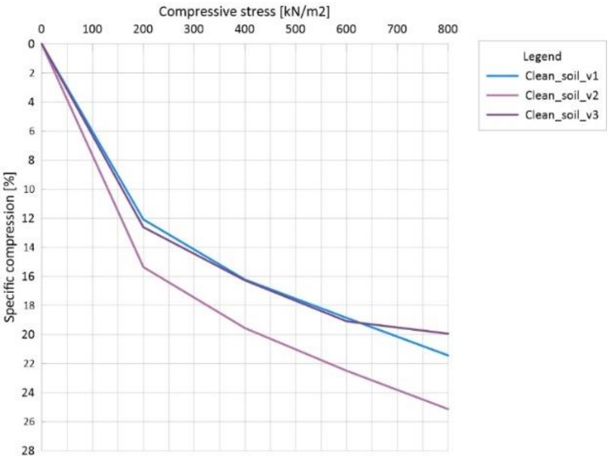
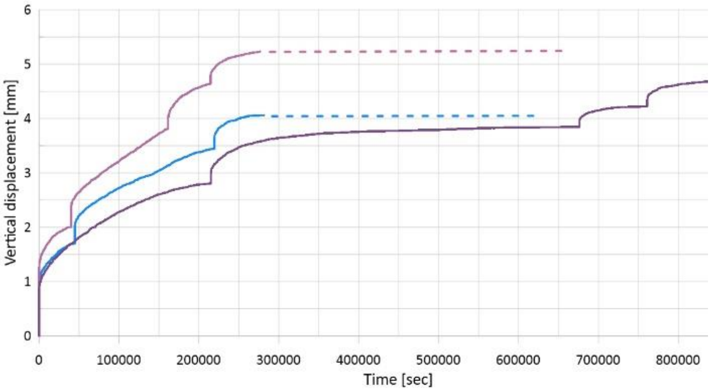


Figure 5. *Specific deformation curves of clean soil samples*

3.3. Test results for contaminated samples

As mentioned in the previous chapter, the contaminated samples were contaminated with 50 w/w% modeling agent (detergent) and then, after one month of undisturbed condition, they were consolidated according to the same methodology as for the clean samples.



* Note: For v1, due to a measurement error, the last load step has not been recorded

Figure 6. *Representation of vertical deformation as a function of time elapsed in contaminated soil samples.*

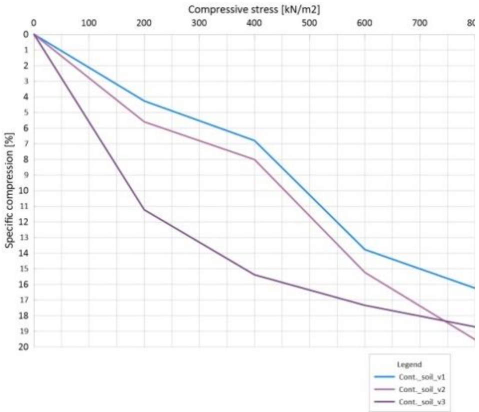


Figure 7. *Specific deformation curves of contaminated soil samples*

3.4. Comparison of the results

If we only plot the time-displacement curves of the raw data, the clean and the contaminated samples in one system, it will be clear that much more time is needed for the contaminated samples to eliminate the excess pore water pressure in the sample.

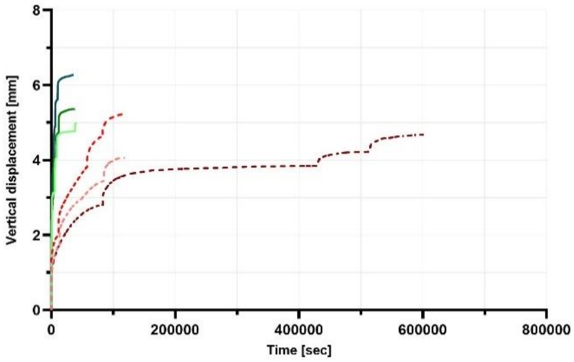


Figure 8. *Representation of vertical deformation as a function of time elapsed in the clean and contaminated soil samples*

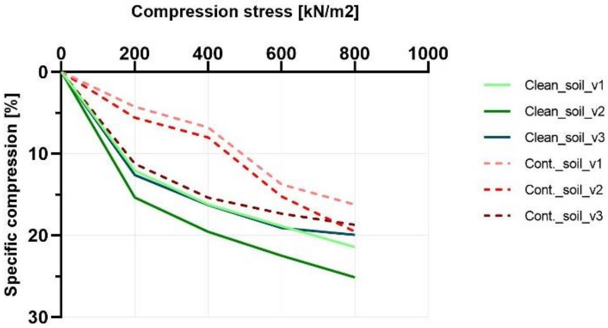


Figure 9. *Specific deformation curves of clean and contamintated soil samples*

Figure 8 shows that the previously emphasized changes can also be observed in the specific deformation curves. Higher specific compression values appear for pure samples than for contaminated samples. This suggests (also based on previous literature research) that detergent appears as a lubricant on the surface of the particles, resulting in an increased degree of consolidation of contaminated samples. (It is worth noting here that in the measurements of hydrocarbon by Safehian et al. (Safehian et al., 2018), this increase in consolidation was attributed to a decrease in the specific surface area of the particles due to contamination and the formation of a shell-like layer around the particle – based on scanning electron microscope (SEM studies). Thus, it can be assumed that this may be a similar phenomenon for the detergent contaminant, but a subsequent SEM test would be more reliable.

The compression curves plotted during the interpretation of the results can be used to interpret the compressibility modulus of the soil, which is the stress associated with a unit specific compression. Differences between these modules were identified as a set of test data. With the help of analysis of variance (ANOVA), we are looking for the answer to the question of whether the presence of contaminant (detergent) affects this modulus. Calculation of compressibility modulus based on readings from the graph is the following:

$$E_s = \frac{\Delta\sigma}{\Delta\varepsilon}; \qquad (2)$$

where:

$\Delta\sigma$: change in vertical stress [kN/m^2]

$\Delta\varepsilon$: change in specific compression [-]

With the help of the analysis of variance, it becomes possible to delimit the systematic factors that statistically actually influence the given data set (rather than the random factors). In practice, this means that the method makes it possible to identify the relationship between different groups. The result of the analysis is the so-called F-ratio, which allows the interpretation of samples as well as differences within samples.

Table 1. *Compressibility modulus for clean and contaminated samples with modified values*

Sample no.	**(E_S) Compressibility modulus [kN/m^2]**	**(E_S) Compressibility modulus [MPa]**
Clean_soil_v1	1666	1,666
Clean_soil_v2	1298	1,298
Clean_soil_v3	1595	1,595
*Clean_soil_v4	1630,5	1,630
Cont._soil_v1	3937	3,937
Cont._soil_v2	3296	3,296
Cont._soil_v3	1781	1,781
*Cont._soil_v4	3616,5	3,616

The table shows that there is an "outlier" between both clean and contaminated samples, which is presumably due to the difference in preparation the sample body. Although the measurements are made from the same sample material and the measurement methodology itself is the same, differences may occur during sample incorporation. Because it is installed in the confining rings manually, a sample of different weights / heights may not be installed. Thus, to avoid the resulting error when running the analysis of variance, the measurement was repeated once more, and the outlier values were not considered (*Clean/Con._soil_v4). The compressibility values of this re-measurement are indicated in *Table 1.*

The equality of the standard deviations can be examined using the F-test to find out whether the difference between our two groups (pure and contaminated samples) is significant or not. Based on the ANOVA test, there is a significant difference between the F-ratio and the value of the 5% inverse function of F (in practice it is worth comparing with this value). This suggests that there is a systematic factor in the system, in this case the presence of detergent, that statistically actually affects the data set (rather than just a random factor).

4. Summary

One of the major groups of anthropogenic contaminants entering the soil is detergents. Although due to their solubility in water, the process of soil remediation is perhaps a less complex problem than e.g., in the case of hydrocarbons, they can still cause significant changes in the different properties of the soil. The aim of this series of measurements is to investigate the effect of the presence of a given detergent model on the consolidation of a clayey soil.

Consolidation studies were performed using an oedometer on 3 clean and 3 contaminated samples. Already during the consolidation process, the "real-time" time-displacement graph showed that the contamination had a significant effect on soil consolidation (this was evident from both the nature of the curves and the time of consolidation itself). This difference appeared in the compression modulus values as well.

The one-way analysis of variance (ANOVA) following the measurements further confirmed the fact that the difference (significant difference) is due to the presence of detergent rather than a random factor influencing the data set. In the future, it would be useful to perform analysis of variance for the data set of other laboratory tests (shear, compaction, leakage factor, consistency limit, etc.). Also, in the near future, the aim is to perform test series on two other types of clay soils and to investigate the effect of another contaminant (hydrocarbon) on all three soils with the same measurements. Furthermore, the time of pollution can also be an important factor (pollutants of different durations).

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