Thixotropy: The Case of Mexico City Soils

J. Abraham Díaz-Rodríguez
Civil Engineering Department, National University of Mexico, MEXICO

J. Carlos Santamarina
Georgia Institute of Technology, Atlanta, GA 30332, USA

ABSTRACT: Thixotropy implies non-equilibrium initial conditions after remolding. At the macroscale, thixotropy manifests as the regain in mechanical properties. At the microscale, thixotropy involves phenomena such as contact creep and interparticle force redistribution, homogenization of pore pressure (in saturated and partially saturated soils), altered ionic distribution and mobility, and the effects of the loose finer fraction. Low-energy thermal or mechanical agitation helps overcome energy barriers at the microscale, favoring the evolution of thixotropic phenomena. Mexico City soils exhibit significant thixotropic effects; the regain in mechanical parameters is accompanied by changes in electrical properties.

KEYWORDS: aging, clays, restoration, structuration, microscale

1 THE MEXICO BASIN

The Cuenca de México (Mexico Basin) is predominantly a flat lacustrine plain at an average elevation of 2250 m. The Basin is surrounded by mountain ranges. It was open until 600000 years ago when volcanic activity during the Quaternary Epoch closed the Basin, resulting in the formation of six principal lakes. The Basin remained closed until 1789 when the lake-water was drained.

Weathered rocks, residual clays, pyroclastic materials, gravels and sands were gradually eroded and the finest elements were transported into the basin. In addition, steam explosions during volcanic eruptions formed dense clouds of fine volcanic ash and other pyroclastic materials which were deposited as a rain on the lake surface (Zeevaert, 1982). Part of the fine volcanic ash recrystallized into clay minerals. The lake sediments also contain a large amount of ostracod and diatom remains (Diaz-Rodriguez, et al., 1998). The latter gives a porous structure to the soil, and very high void ratio.

This paper starts with a review of salient aspects of Mexico City soils. Then, the phenomenon of thixotropy is analyzed into multiple possible mechanisms. The paper ends with an exploratory experimental study of thixotropic changes in Mexico City soils.

2 MEXICO CITY SOILS

The following list of properties highlights the unique characteristics of Mexico City Soils (Díaz-Rodríguez, et al. 1989, 1992, 1997; Mesri et al. 1975; Zeevaert, 1982): plasticity index 300%; water content 400%; electrical resistivity ~10 Ohm-m; hydraulic conductivity ~10^{-8} cm/s; minerals 14 Å montmorillonite, illite and cristobalite; cation exchange capacity ~0.9 meq/g; friction angle 42°-47°; coef. earth pressure at rest 0.3; compression coefficient ~10; almost constant shear modulus and damping less than 4% for shear strains as high as 1%; velocity-stress exponent 0.11 (in situ); no strength loss even when the amplitude of the dynamic cycles is as high as 80% of the quasi-static strength.

One of the most astonishing properties of Mexico City clays is the remarkable regain in strength and deformation properties with time after remolding. This phenomenon is referred to as thixotropy.

3 THIXOTROPY - MICROSCALE

Originally, the term thixotropy implied the reversible and isothermal solid-liquid transition (gel-sol) of colloidal systems upon mechanical excitation. However, this definition has been generalized. In soil mechanics, there are several related terms: aging, thixotropic aging, restoration, structuration, and cold welding, among others. Clear semantic or physical distinctions among these terms are difficult to establish. Furthermore, while thixotropic-like behavior has been observed in various soils around the world, it has seldom been analyzed into its underlying causal mechanisms.

Research results in the clay mineralogy literature show the association between thixotropic behavior and flocculation prone clay systems (see Van Olphen, 1951). Mixtures with low ionic concentration immediately set into a gel, however, time dependent thixotropic hardening manifests in suspensions with high ionic concentration that tend to form flocculated structures. Research in soil mechanics confirmed the importance of flocculation on thixotropic behavior (Mitchell, 1960. Note: a comprehensive list of references can be downloaded from the authors web site, including references to multiple related studies by Mitchell and co-workers).

Time-dependent changes highlight non-equilibrium conditions after the application of shear. These cause gradients of chemical, electrical, mechanical or thermal origin. In order for time-dependent effects to manifest, the time scale for the equilibrating process must be significantly longer than standard laboratory measurements, which are usually in the order of minutes. Therefore, hypotheses about thixotropy must also consider possible retardation mechanisms that can contribute to the observed time-dependent regain in material properties.

Several microscale phenomena are analyzed in this section, as potential contributors to the general phenomenon of thixotropy. We address those mechanical and chemical processes that can explain reversible time-dependent hardening. In this review, macroscale boundary criteria (such as isothermal, constant composition, and constant volume) are not required at the microscale. In other words, local thermal, chemical, mechanical or electrical transport can take place.

3.1 Interparticle force redistribution - Creep

The macroscale phenomenon of stress corresponds to an internal distribution of interparticle contacts and interparticle normal and shear forces. Thus, thixotropy should either cause changes or be the result-of changes in interparticle forces.

An experimental study with photoelastic disks was conducted with a random assembly of 12 mm and 25 mm disks, loaded under zero lateral strain conditions. A close up view of a few disks is presented in Figure 1.

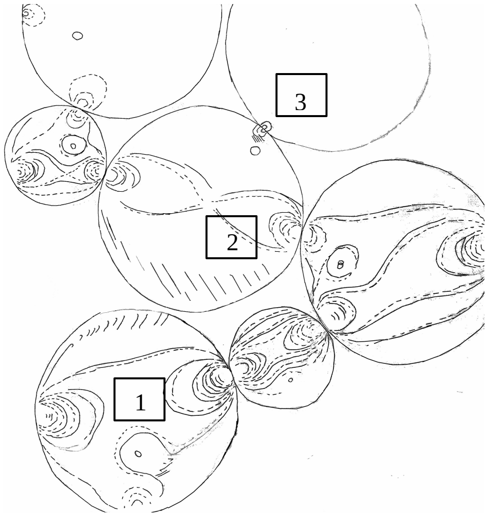

Figure 1. Force and fabric changes due to creep within particles

The doted lines correspond to fringes observed immediately after loading, while the continuous lines denote the fringes observed 3 weeks after loading. The following changes are noticed: (1) variations in normal force, (2) changes in shear force -denoted by the change in the symmetry of fringes relative to the contact normal, (3) formation of new contacts, i.e., increase in coordination number. In general, the fastest changes take place in the most highly loaded contacts, which are along the principal chains of forces. Similar mechanisms are expected in fine-grained platy particles, such as clays, although these phenomena may take place at the intermediate scale of granularities.

Results from numerical micromechanical simulations confirm these observations. Kuhn and Mitchell (1993) considered creep only on the tangential component of the contact force. Rothenburg (1992) considered creep in both normal and tangential components. While specific results reflect the assumed model for contact behavior, both studies agree that the wider the variability in contact forces, the higher the creep rate.

Contact force redistribution, increase in coordination, and contact flattening during creep give rise to a significant increase in small strain stiffness, as it has been experimentally shown (Cascante and Santamarina, 1996; Santamarina and Aloufi, 1999).

These changes are restricted by the minimum activation energy required for the processes involved, such as material creep within grains and friction at contacts. In fact, the very soft Mexico City soils exhibit a low value of $k_o \approx 0.3$.

3.2 Non-Uniform Pore Pressure Distribution

While most observations on thixotropy are based on low solids-concentration gels, thixotropic effects have also been observed in fairly dense kaolins and bentonites in the context of stiffness loss-and-regain following zero-lateral-strain loading in an oedometer cell (Figure 2).

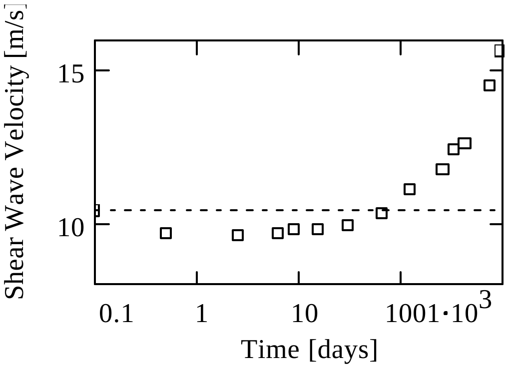

Figure 2. Stiffness recovery after disturbance. Saturated bentonite specimen in rigid oedometer (vertical stress was increased from 10 to 100 kPa).

Santamarina and Fam (1995) hypothesized several mechanisms, including the generation of non-homogeneous pore pressure throughout the soil mass, and its subsequent redistribution and homogenization. Given the non-linear behavior of particulate materials, a homogeneous pore pressure renders higher stiffness than a heterogeneous pore pressure field (with the same stress boundary conditions in both cases). Such a situation can develop in dual porosity media. Secondary consolidation can also be explained in this context.

While remolding involves moisture migration to shear zones, moisture homogenization after remolding involve fluid flow away from the shear zones. Mitchell (1960) used the changes in the rate of thixotropic regain with temperature to estimate the activation energy of the process. The computed values of 3-4 kcal/mol suggest that the viscous flow of water is the main underlying mechanism.

3.3 Partially Saturated Materials

Stiffness recovery has been observed in partially saturated materials after they have been disturbed from at rest conditions. At equilibrium, the negative pore pressure experienced in the fluid is constant throughout the mass (within a scale that permits disregarding effects such as gravity). This negative fluid pressure alters the effective stress and resultant properties, in particular the small-strain stiffness. However, when the medium is disturbed by an excitation that causes strains usually above the threshold strain, menisci and pore fluid distribution are altered, so is the stiffness of the soil mass.

Two different regions of partial saturation are identified. In the funicular region, the water phase is interconnected (medium and high saturation). In this case, recovery involves pore pressure redistribution and fluid motion within the continuous fluid phase. The rate of recovery is controlled by permeability, and full-recovery is usually possible (Figure 3 - based on experimental data presented in Cho and Santamarina, 1999). In the pendular region, the fluid phase is not continuos (low saturation). Water is only present within menisci at contacts, and the vapor pressure which is related to the curvature of menisci, is responsible for homogenizing the fluid pressure at different contacts. This is a slow process. Furthermore, if the degree of saturation is small enough, the rupture of a meniscus leads to the redistribution of the fluid on the particle surface and the meniscus may not re-generate even if particles return to contact. Therefore, the time-dependent recovery of stiffness in partially saturated soils within the pendular region is slow, and may not be complete (Figure 3).

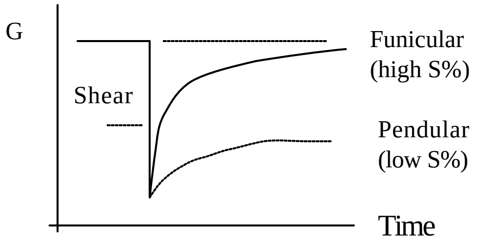

Figure 3. Stiffness regain in partially saturated soils

Mitchell (1993) reports results by P.R. Day whereby tensiometers where embedded in day pastes (apparently saturated), allowed to reach equilibrium, followed by the mixing of the clay. Tension decreased immediately after mixing and recovered with time. Besides the mechanisms described above, these results may reflect the entrapment of gas and its time dependent diffusion. In addition, ionic movement after mixing may cause particle rearrangement.

3.4 Coagulation

Depending on interparticle distance, ion valence and ionic concentration, two contiguous particles may experience an attraction resultant force between double layer repulsion and van der Waals attraction, promoting coagulation (there are other important environment variables such as pH, and forces such as hydration forces). Edge-to-face connectivity is affected by ionic concentration and valance as well: as the double layer shrinks, edge charges are exposed and the development of edge-face contacts is facilitated.

The time scale of coagulation depends on ion movement (which is diffusion controlled) and particle mobility (which is viscosity controlled). The rate of these changes increases as temperature increases.

While coagulation implies particle movement δ, changes in interparticle distance in the order of nanometer are sufficient. The lower the specific surface of a clay S_S and the higher the void ratio e_o, the lesser the effect of this displacement on the global strain ε. For parallel particles,

$$\varepsilon = \delta \frac{S_s \cdot \gamma_w \cdot G_s}{2(1+e_o)} \qquad (1)$$

For example, a global interparticle displacement of 1 nm in a soil with $S_S \approx 10$ m^2/gr and e=1.0 causes a global strain smaller than 10^{-3}. Furthermore, when coagulation occurs at the level of the mobile particles in a soil mass, it causes no global strain, yet the increase in stiffness may be significant.

3.5 Mobile and Fixed Particles

Visualizations of granular assemblies highlight the connectivity of particles (the "fixed" fraction). However, simple experiments with random assemblies of disks clearly show a large percentage of particles that do not directly contribute to the transmission of load through the soil skeleton (the "mobile" fraction). This situation is heightened in gap-graded materials where the finer fraction is not sufficient to fill the voids left by the coarser fraction. In this case, the fines are held in position by gravity and other interparticle forces (e.g., electrical, capillary).

While the coarser fraction that forms the skeleton experiences its own thixotropic effects (such as creep discussed above), the mobile finer fraction gradually assembles around the coarser particles. These particles stiffen contacts and stabilize the coarse-grain skeleton preventing buckling. The result is a stiffer soil with a higher threshold strain. Capillary forces facilitate the alignment of particles around contacts during drying. Clay bridges and buttresses in loess are a salient example. Osipov, et al. (1984) showed the restoration of the microfabric during thixotropic recovery, including the re-generation of clay bridges. Thus, the thixotropic effects of the mobile fraction may justify, at least in part, the experimental observations whereby some materials appear to gain or recover their structure with time.

3.6 Low Amplitude Vibrations - Temperature

Experimental results show that low amplitude vibrations can accelerate thixotropic effects; this phenomenon is called rheopexy in the context of clays and cyclic pre-straining in the context of sands. What are the possible internal mechanisms underlying rheopexy and cyclic pre-straining?

Consider a stable soil under constant boundary conditions. From an energy point of view, the medium is at the bottom of an energy well, and any change will require overcoming some energy threshold. At the microscale of contacts, there is a frictional threshold at each contact stopping further slippage. Likewise, there is an energy threshold at the molecular scale restricting movement (this is relevant to the monolayers closest to the mineral surface; for clarity, imagine dragging a cation parallel to a negatively charged mineral surface: successive energy wells would be encountered in front of each negative charge).

Vibration externally applied to the soil may contribute to overcoming the corresponding energy barriers, triggering internal changes (the associated phenomenon of "stochastic resonance" is addressed in a current report by Wang and Santamarina). Once the process is triggered, internally liberated energy, for example in the form of acoustic emission, may contribute to sustain the process of change until a new energy well is reached.

Low frequency vibrations are large wave-length phenomena with respect to the particle size. However, temperature is a measure of vibration level, in this case at the molecular level. Therefore, analogous effects are attained at the molecular scale by increasing temperature (atomistic simulations confirm this observation).

While this mechanism violates the isothermal criterion attached to thixotropic phenomena, background vibration and above absolute-zero temperatures are physical realities in all engineering soil environments.

3.7 Solution, Precipitation, Cementation

Solubility depends on pressure (and temperature): the higher the pressure, the higher the solubility. Therefore, the high pressure at interparticle contacts tends to favor the solubility of the particle near the contact. The hydrated phase diffuses to the boundary of the contact where it precipitates. The final effect is the formation of a wider, more stable contact rendering a stiffer medium. If the process is massive, as in granular salt, volumetric reduction may be observed at the macroscale. Still, this is a constant composition phenomenon from a boundary point of view. This phenomenon takes place in all minerals, including quartz (some polymorphs are much more soluble than quartz at 25C; furthermore, alkali ions such as sodium increase solubility).

Cementation may develop in different forms, including ionic bonding (e.g., through a shared divalent cation), clay bridges and buttresses, salt precipitation in partially saturated materials (salts precipitate at contacts when the ionic concentration in menisci reaches the saturation level during drying), pozzolanic effects (aluminates, silicates, carbonates).

Lessard and Mitchell (1985) identified a sequence of processes leading to the aging of quick clays, involving oxidation, acidification, dissolution, and ion exchange. While the sequence is irreversible, conditions achieved at a given stage may be altered during remolding, to be further continued after remolding. Furthermore, these phenomena may be involved in laboratory studies of thixotropy.

4 MACROSCALE - MEXICO CITY SOILS

Macroscale observations related to the effect of thixotropy on soil properties include:

- Increase in low strain stiffness.

- Decrease in early contractive tendency (thus, a decrease in early pore pressure build-up).
- Increase in quasi-preconsolidation stress (a function of PI).
- Increase in permeability.
- Limited or no effect on effective strength parameters.

It is worth noting that aging and cementation cause similar effects.

A study of the thixotropic response of Mexico City soils was conducted with specimens obtained from a site located in the ancient lacustrine zone of Mexico City, at the Alameda Central (19.26°N, 99.08°W). This is situated near one of the most damaged areas during the September 19, 1985 earthquake. The samples were recovered with a Shelby tube (12.5 cm in diameter), from a depth of 24 m. The water content is w=240%, the liquid limit is LL=399%, and the plastic limit PL= 76%. The experimental study follows.

4.1 Large Strain Mechanical Properties

The unconfined compression test and the fall cone test were used as comparative measurements to assess the time-dependent strength changes. Cylindrical specimens (H/d=2) were prepared from a remolded sample at the natural water content. Specimens were sealed and stored.

The unconfined compression load-deformation data are shown in Figure 4.

Both strength and stiffness increase with time. The natural undisturbed Mexico City samples present the highest values. Strength is plotted vs. aging time in Figure 5. The increase in strength follows an exponential relation. Unfortunately, no measurement of pore pressure is available, therefore we cannot verify that the effective stress strength parameters remained constant. Should this be the case, the change in water tension must be in the order of:

$$\Delta u \approx \Delta q \frac{1-\sin\phi}{2\cdot\sin\phi} \qquad (2)$$

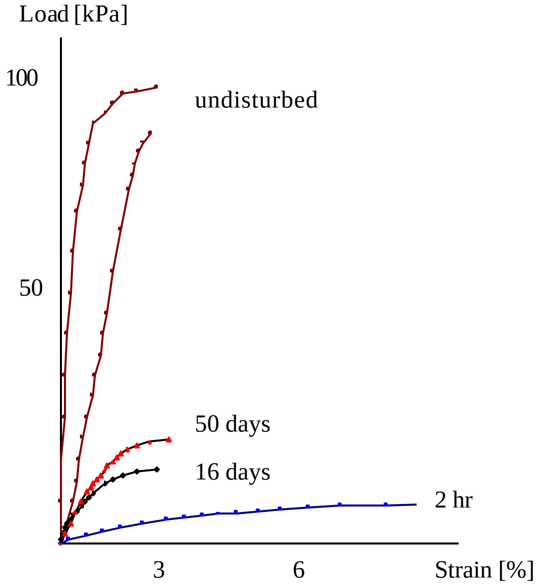

Figure 4. Load-deformation in unconfined compression. Undisturbed and remolded specimens with different aging time

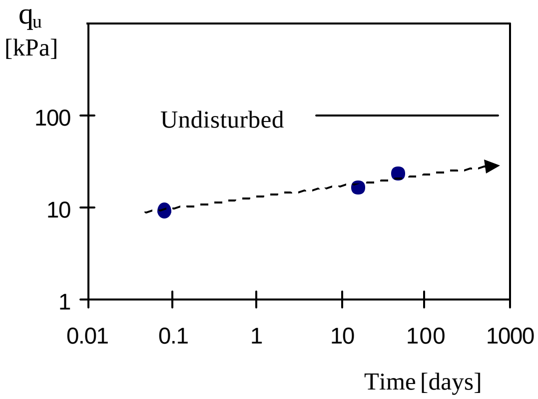

Figure 5. Evolution of unconfined compression strength with time

The fall cone test was run with different static loads. Test results are shown in Figure 6. Once again, an exponential increase in strength is obtained. The values for the undisturbed specimen are shown as well.

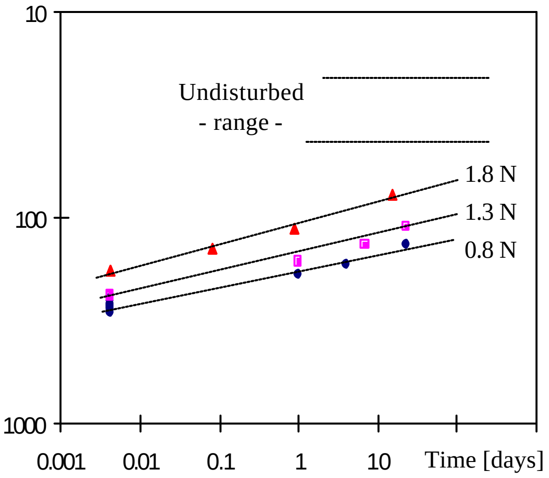

Figure 6. Penetration of the fall-cone [0.1mm] vs time for different static loads.

4.2 Small Strain Dynamic Properties

Laboratory studies still in progress show the unequivocal effects of aging on low-strain stiffness and attenuation in Mexico City soils. In particular, attenuation shows a sudden increase when the static load is changed, recovering afterwards. Similar observations were made with materials that present contact creep and re-crystallization such as pressure solution-precipitation (e.g., granular salt and lead shot; Cascante and Santamarina, 1996).

4.3 Electrical Properties

Given the dependency of electrolytes on thixotropic behavior, it is not surprising that changes in conductivity and permittivity should be observed during thixotropic changes. Changes in complex permittivity after remolding for a Mexico City specimen are shown in Figure 7.

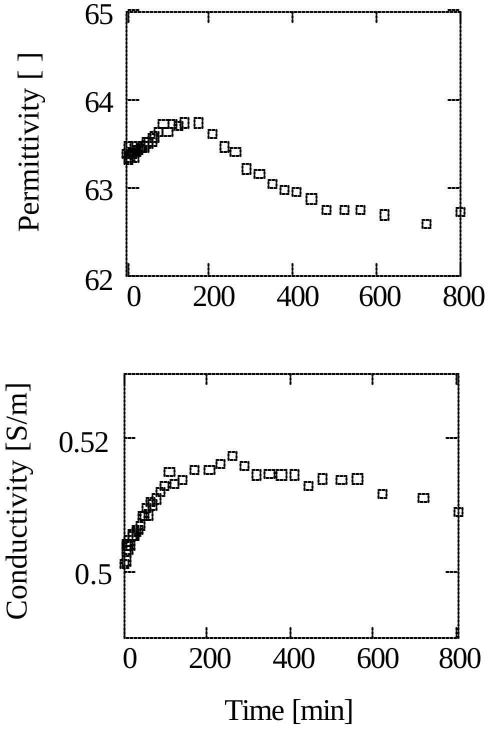

Figure 7. Evolution of electrical properties after remolding. Mexico City soil specimen. Real relative permittivity and effective conductivity measured at 0.2 GHz.

The peaks in permittivity and effective conductivity are reached at about the same time. The spectrum (not shown) suggests interfacial polarization, i.e., the changes in conductivity cause the changes in permittivity. Thus, the underlying internal mechanisms must be associated to changes in ionic mobility within the fluid and adsorbed layers.

Note that the alteration in electrical properties lasts a fairly short period of time, as compared to the long-term continuous increase in mechanical properties. Therefore, more than one mechanism appears to contribute to the thixotropic characteristics of Mexico City soils.

5 FINAL COMMENTS

Mexico City soils are unique in many aspects, including strong thixotropy. Non-equilibrium initial conditions after the application of shear lead to time-dependent "thixotropic" changes (at virtually zero energy flux across the boundary). Changes include: increase in stiffness, decrease in early contractive tendency, and increase in undrained shear strength (however, effective strength residual parameters appear to remain unaltered).

Several micro-scale phenomena are identified as potential contributors to the phenomenon of thixotropy: contact creep, interparticle force redistribution, non uniform pore pressure distribution in saturated and partially saturated soils, alteration in ionic distribution and mobility, the ensuing changes in interparticle forces, and the mobility of the finer fraction in the soil mass. Agitation (thermal or mechanical) helps overcome energy barriers at the microscale and facilitates thixotropic recovery.

ACKNOWLEDGEMENTS

We are grateful to D. Fratta, K. Klein, L. López-Flores, G. Ruíz-Bautista, and V. Vandolas. Concepts presented above matured through discussions in the "Clay Club", an electronic forum on clays. The monitoring of thixotropy with electrical measurements was first shown by V. Rinaldi in this forum (UNC, Argentina).

REFERENCES

(Note: an extended list of references can be found in association with this publication in www.ce.gatech.edu/~carlos/).

Cascante, G. and Santamarina, J.C. (1996) Interparticle Contact Behavior and Wave Propagation, ASCE Geotechnical Journal, vol. 122, no. 10, pp. 831-839.

Cho, G.C., and Santamarina, J.C., Partially Saturated Particulate Materials - Particle level studies, (Under review, available from the authors).

Díaz Rodríguez, J.A. (1989) Behavior of Mexico City Clay Subjected to Undrained Repeated Loading, Canadian Geotechnical Journal, Vol. 26 (1) : 159-162.

Díaz Rodríguez, J.A., Leroueil, S. and Alemán, J.D. (1992) On yielding of Mexico City clay and other Natural clays, Journal of Geotechnical Engineering, ASCE, Vol. 117 (7): 981-995.

Díaz Rodríguez, J. A. y López Flores, L. (1997) Effect of soil microstructure on the dynamic properties of Mexico City clay, XIV International Conference on Soil Mechanics and Foundation Engineering, Hamburgo, Alemania.

Díaz-Rodríguez, J.A., R. Lozano-Santa Cruz, V.M., Dávila Alcocer, E. Vallejo, and P. Girón. 1998, Physical, chemical and mineralogical properties of Mexico City sediments: A geotechnical perspective. Canadian Geotechnical Journal 35, pp. 600-610.

Kuhn, M. R. and Mitchell, J.K. (1993) New Perspectives on Soil Creep, ASCE J. Geotechnical Engineering, 119(3): 507-524.

Lessard, G. and Mitchell, J.K. (1985)"The causes and effects of aging in quick clays". Canadian Geotechnical Jounal 22 (3) : 335-346.

Mesri, G., Rokhsar, A. and Bohor, B.F. (1975) Composition and compressibility of Typical Samples of Mexico City Clay, Geotechnique, vol. 25, 527-554.

Mitchell, J.K. (1960) Fundamentals aspects of thixotropy in soils. Journal of the Soil Mechanics and Foundations Division, ASCE, 86 (3) :19-52.

Mitchell, J. K. (1993) Fundamentals of Soil Behavior, Second Edition, Wiley, New York.

Osipov, V.I., Nikolaeva, S.K. and Sokolov, V.N. (1984) "Microstructural changes associated with thixotropic phenomena in clay soils". Géotechnique 34, pp. 293-303.

Rothenburg, L. (1992) Effects of Particle Shape and Creep in Contacts on Micromechanical Behavior of Simulated Sintered Granular Media. ASME MD-vol. 37, Mechanics of Granular Materials and Powder Systems, pp. 133-142.

Santamarina, J.C., and Fam, M. (1995) Changes in Dielectric Permittivity and Shear Wave Velocity During Concentration Diffusion, Canadian Geotechnical Journal, vol. 32, no. 4, 647-659.

Santamarina, J.C. and Aloufi, M. (1999) "Micro-scale Interpretation of Wave Propagation in Soils -Fabric and Fabric Changes-", IST99, Torino, Italy.

Van Olphen, H. (1951) Rheological Phenomena of Clay Sols in Connection with the Large Distribution of Micelles, Discussions of the Faraday Society, no. 11, pp. 82-84. (additional information in his book)

Zeevaert, L (1982) Foundation Engineering for Difficult Subsoil Conditions, 2nd Ed. Van Nosrand-Reinhold Co., New York, NY.