SUCTION RESPONSES DUE TO HOMOGENEOUS SHEAR OF DILUTE MONTMORILLONITE–WATER PASTES*

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ABSTRACT

A RECENTLY described phenomenon, the shear induced decrease of moisture suction in saturated clay–water systems and its subsequent recovery, has been investigated with the aid of a parallel plate shearing device. The apparatus allowed a more quantitative description of the phenomenon than was previously possible. In 4–6% Na-montmorillonite pastes it demonstrated a well defined suction response to shear even for shear angles as small as one degree. The observed decrease in suction was rapid at first. It terminated within a few minutes and was followed by an approximately exponential, occasionally incomplete recovery. All the tests carried out exhibited the same general features of suction change.

It is postulated that shear induces a displacement or change in configuration of particles and that subsequently they return to their original states due to thermal motion. The shapes of the recovery curves can be interpreted in terms of the relaxation spectrum functions encountered in linear viscoelasticity theory. By utilizing a characteristic relaxation time for these spectra, rate process theory has been employed to interpret the bonding mechanism in terms of the experimental activation free energy. The results suggest that the bonds which are re-established during the recovery are primarily of the Coulombic type.

Shear induced suction changes should be considered when dealing with deformation theories and structural models of wet soils and clays. Indeed they provide a means of testing certain aspects of soil structure.

INTRODUCTION

THE changes of soil moisture suction brought about by shear were reported by Day (1954–56), and have been discussed in a recent paper by Day and Ripple (1966). The effects are closely related to the phenomenon of thixotropy, defined by Burgers and Scott Blair (1948) as a process "of softening caused by remolding, followed by a time-dependent return to the original harder state". The suction was found to decrease or increase in accordance with the preconsolidation history of the specimen. Samples that had been

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normally consolidated by suction underwent a decrease of suction when sheared, whereas samples that had been strongly overconsolidated experienced an increase of suction. The effects were observed in many kinds of clay–water systems. It was suggested that shear causes rupture or displacement of the structural bonds of the clay–water systems, and perhaps more significantly that the structures tend to reform spontaneously. The purpose of the present work is to examine the recovery process in more detail with special attention to its interpretation by the relaxation theory approach. The experiments described herein are concerned entirely with electrolyte-free dilute sodium bentonite suspensions, having suctions in the order of 1–3 g/cm².

THEORY

The recovery process, which begins immediately after the abrupt change of suction has occurred during shear, has the characteristics of a *relaxation phenomenon*. Maxwell (1867) employed this concept long ago for stress relaxation studies, and his early ideas form the basis of modern linear visco-elasticity theory. One of the salient features of this approach is the relaxation time, which is a characteristic of the recovery process for the particular material. Alfrey and Gurnee (1956) have defined the relaxation time τ in the following manner: " . . . the relaxation time is equal to the time required for the stress to relax to $1/e$ of its initial value when the strain is held constant."

Recent developments in linear viscoelasticity suggest a spectrum of relaxation times for many phenomena. A spectrum consists of a function comprising a number of superposed individual exponential relaxation functions, each characterized by a specific relaxation time. In spite of the fact that a spectrum is often observed, a nominal or "bulk" relaxation time may be estimated from the observation, and this may be assumed to approximate the relaxation time for the dominant component. This point will be discussed in more detail later.

A connection is needed between relaxation theory and rate process theory in order to estimate the bond interaction energies in clay water systems. The original rate process theory for the viscosity and diffusion of liquids, as discussed by Glasstone, Laidler, and Eyring (1941) was concerned with determinations of rate constants and activation free energies by the methods of statistical mechanics.

The theory assumed the existence of "flow units" ("flow patches")—usually molecules—which normally occupy equilibrium positions determined by their interactions with their neighbors. Since many equilibrium positions are actually metastable, the supplying of energy may overcome the energy barrier which separates an occupied energy "well" from an adjacent un-occupied one, causing the transfer of a flow unit from one to the other, and altering the potential energy of the system. The minimum energy necessary to surmount the barrier is called the activation free energy, expressed in energy units per mole of activated complex, or per mole of flow patches.

Shearing stresses are presumed to lower the potential barrier in a direction defined by the stress, and a certain number of flow units are thus able to move from their original site to adjacent "holes" created by the random thermal motion of all of the units. In this manner, the flow units are assumed to be transported in parallel layers, one layer being affected by its adjacent one through viscous drag effects. The outgrowth of this is a rate constant equation for the transported flow units (defined for the case of no stress acting):

$$k' = \kappa \, \frac{kT}{h} \, e^{-\Delta F^{\ddagger}/RT} \tag{1}$$

where κ = transmission coefficient (dimensionless, usually = 1),

k = Boltzmann constant,

T = absolute temperature,

h = Planck's constant,

$\Delta F^{\ddagger}$ = activation free energy for flow (kcal/mole),

R = gas constant per mole (kcal/degree/mole).

Ree and Eyring (1958) have developed a generalized theory of viscosity based upon rate process theory. They define the relaxation time of a flow unit "as the reciprocal of the rate constant for the flow of the unit, i.e. $1/k'''$". A relation that actually evolves from the rate process equations for viscosity is

$$\frac{1}{k'} = \beta\left(\frac{2\lambda}{\lambda_1}\right) \tag{2}$$

where λ_1 = distance between flow layers,

λ = distance between two equilibrium positions in the direction of shear.

As Ree and Eyring point out, β alone of this equation may be used as equivalent to the relaxation time, since it is essentially that quantity multiplied by a dimensionless constant "probably not differing much from unity". Hence, the following relation may be assumed, connecting the relaxation times of rate process theory and linear viscoelasticity.

$$\tau = \frac{1}{k'} \simeq \beta \tag{3}$$

In the present case, this equation simply assumes that the rate of relaxation, as measured by a stress parameter (the suction), is determined by the rate at which the random transporting of flow units occurs under the influence of thermal motion (i.e. the rate at which holes are filled and reformed elsewhere in the system). From this and equation (1) the working relationship may be expressed by

$$\tau = \frac{h}{kT} \, e^{\Delta F^{\ddagger}/RT} \tag{4}$$

The direct connection between the relaxation time and free energy of activation for viscous flow can furnish information concerning the structural bonding of the system. The basis for this expectation is the plausible assumption that the energy required for hole formation is a function of the bond strength between molecules.

There are certain qualifications that need to be mentioned in advance concerning the applicability of the preceding theory to clay–water systems. In the first place, it is assumed that the theory is applicable on the macromolecular level. The size of the flow unit, whether it consists of a single clay particle or a cluster of them, is much greater than in ordinary liquids. However, Ree and Eyring have considered the heterogeneous nature of flow units in such materials as rubber, and other polymers. They conceive of the flow units as consisting of single molecules, segments of polymerized molecules, or even groups of molecules. These are also subject to various degrees of entanglement, or type and degree of bonding. Similarly, it may be assumed that the flow units in a clay–water system are polydisperse, and that their sizes may be arbitrarily classified into dominant groups, each characterized by an average relaxation time.

A generalized concept of a "hole" is called for in discussing the deformation of wet clay. The very nature of the clay particles, with their surrounding force fields pervading the water of the system would seem to describe a complex system of equilibrium positions. Each clay particle could be thought of as being surrounded by a much convoluted equipotential surface. This surface would describe both the dimensions of the flow unit and the many equilibrium positions. Thus, the concept of a "hole", an easily grasped concept for an ideal liquid and essential to the rate process theory, may be thought of in the case of clays as merely an adjacent equilibrium position, or configuration.

Finally, special attention must be given to the use of the relaxation time concept for clay–water systems. Shuler and co-workers (1959, 1962) have pointed out that the simple relaxation law yielding a monotone exponential function does not hold in general. The relaxation dynamics are generally too complicated for this simple interpretation. More specifically, viscoelastic systems are generally characterized by relaxation spectra having a number of superimposed, discrete, relaxation times (Marvin, 1962). Nevertheless, the influence of the dominant components acting in the process can be assessed qualitatively from estimates of the average, or "bulk" relaxation time.

APPARATUS AND PROCEDURE

The materials used in this experiment were restricted to an arbitrarily prepared form of bentonite. The bentonite (American Colloid Co., KWK Volclay) was dispersed in water as obtained from the supplier, and the $< 2\ \mu$ fraction siphoned off. This material, of approximately 1.5% concentration, was then passed rapidly and continuously through a series of resin exchange columns (H, OH, H, and Na in that order) after a method of

Carlson (1962) and Barshad (1962). In this way an essentially electrolyte-free, homoionic Na-montmorillonite was prepared. The suspension was then reduced in water content by gentle heating accompanied by stirring (80°–85°C) to about 3–3.5% concentration. At this point, the material was subjected to a vacuum distillation (maintained at 70° C) until the sample reached the desired water content. It was then stored under vacuum in the constant temperature testing room (25.0°–25.5°C) until use. This technique is entirely equivalent (but produces a more uniform clay paste) to desorption by suction and also results in a normally consolidated specimen as mentioned earlier.

The shearing tests on the clay–water specimens were conducted in a parallel plate shearing device described by Ripple (1965). The great advantage of this device is the fact that all parts of the specimen are subjected simultaneously to equal amounts of shear (homogeneous strain).

The device consisted of a base assembly, supporting a rectangular sintered glass plate, on which the sample was placed. A mating frosted glass plate formed the upper parallel boundary for the clay paste, and was suspended from a movable carriage assembly allowing transverse motion. The lower sintered plate was connected by stainless steel tubing to a Sanborn Model 268 B pressure transducer, and the suction responses recorded with the aid of a Sanborn Model 140 B amplifier and Model 127 Recorder. Suction changes on the order of 0.01 g/cm^2 of water were readily detected in this system with a volume displacement of only 3.85×10^{-3} mm^3 for a pressure change of 1 g/cm^2.

Great care was taken to prevent temperature fluctuations and evaporation losses. The entire test apparatus was housed in a constant temperature room with an ambient temperature drift of usually no more than 0.1°C per 24 hr. The actual test apparatus was then further surrounded by an insulated chamber, through which was circulated high relative humidity air (90% R.H.) of even greater temperature stability. The temperature of the test apparatus itself was usually well within < 0.05°C per 24 hr. Most of the testing was carried out at nominal temperature of 25.5°C. Moisture losses were reduced as much as possible by the maintenance of a high relative humidity in the air surrounding the test apparatus. A water vapor barrier, consisting of a viscous mixture of mineral oil and petroleum jelly, was placed around the edges of the sample and around the seal between the sintered glass plate and the lower holder. Also, nickel seals were used in the all-metal pressure measuring system. In this manner, evaporation losses were prevented from the relatively small volume of specimen (approximately 10 cm^3) which might have otherwise been interpreted as a pressure change.

After the specimen had been installed, a steady state suction was soon reached (approximately 24 hr). The sample was then sheared an arbitrary amount by advancing a screw assembly, imparting a linear motion to the upper assembly and consequently a shearing strain to the sample. This has been expressed by the angle of shear γ, defined as the angular displacement, from the vertical, of a linear array of particles that had initially occupied a

line perpendicular to the plane of shear, the latter being parallel to the plates. The linear displacement u of the upper plate was measured by means of an optical lever system, and the amount of strain was calculated from the equation $\gamma = \tan^{-1}(u/d)$, where d represents the distance between the plates.

The suction changes resulting from shear were measured by means of the pressure transducer and recording accessories referred to above.

RESULTS

Representative results are given in Figs. 1–3, in the concentration range of 4.52–5.18% (= weight of oven-dry clay (105°C) × 100/weight of water removed). The effect of shear was to produce an immediate decrease of suction, followed by a gradual recovery towards, although not always reaching, the initial value. Measurable decreases of suction were observed for shearing angles as small as 1°. The recovery curves were all similar in shape, though varying in magnitude of change and rate of recovery.

Estimates of bulk relaxation times from the curves of Figs. 1–3 (series 19 B —clay concentration 5.18–4.69%), and some additional ones from series 18 B (clay concentration 4.52%) are given in Table 1. Because they are not simple exponentials, their magnitudes have been estimated by two methods in order to give a more complete representation of the spectrum than provided by a single parameter. The first is the time τ required to reach 63.2% (= 100–100/e) of the final recovery value following shear. The second method is one that had been proposed by Reece (1959), who multiplied the half-amplitude recovery time by 1.37 giving τ'. The agreement between the two
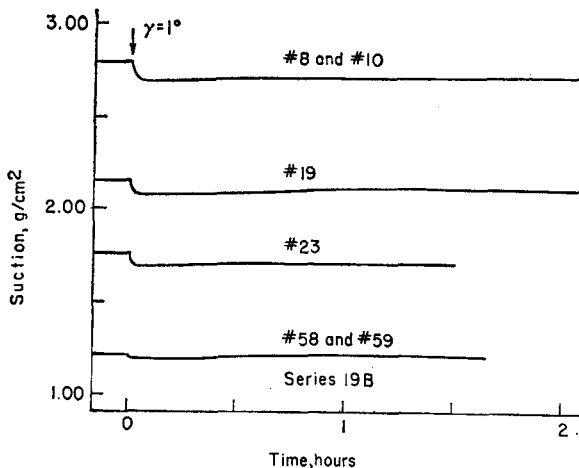

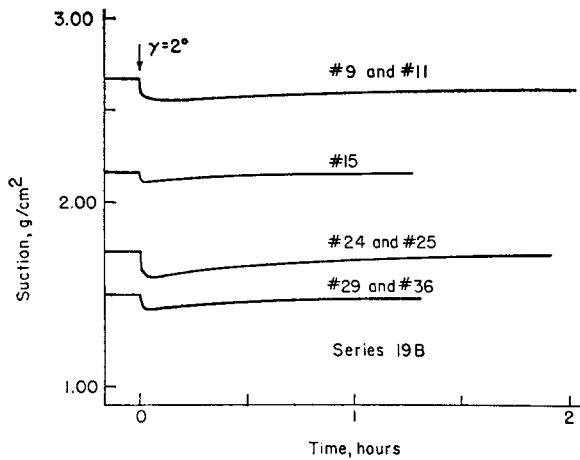FIG. 1. Changes of suction following 1° shear. (< 2 μ Volclay bentonite, Na-form, electrolyte-free.)

FIG. 2. Changes of suction following 2° shear. ($< 2 \mu$ Volclay bentonite, Na-form, electrolyte-free.)
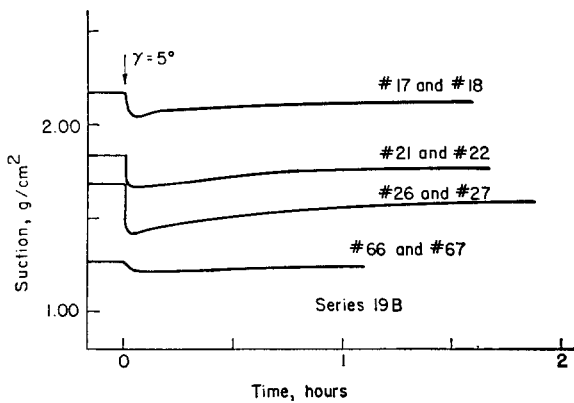

FIG. 3. Changes of suction following 5° shear. ($< 2 \mu$ Volclay bentonite, Na-form, electrolyte-free.)

methods is good enough to suggest that the recovery process is influenced by some dominant component of the polydisperse system.

The relaxation times of Table 1 vary from 20 min to almost 3 hr. However, the corresponding free energies of activation occupy the narrow range of 21–23 kcal/mole, as calculated from equation 4 (see Table 2). These are to be regarded as *experimental free energies of activation*.

Table 1.—Estimated "Bulk" Relaxation Times
For < 2 μ Electrolyte-free Na Bentonite for
Various Amounts of Shear

Series and test numbers	γ (degrees)	τ' (sec)	τ (sec)
19B 8 and 10	1	1.8×10^3	1.8×10^3
19	1	3.5	2.9
23	1	1.8	2 0
58 and 59	1	2.5	2.2
9 and 11	2	3.0	3 3
15	2	1.3	1.2
24 and 25	2	2.5	3.3
29 and 36	2	2.0	2.1
17 and 18	5	1.4	1.8
21 and 22	5	2.1	1.9
26 and 27	5	2.1	2.2
66 and 67	5	2.2	2.4
18B 1	2	4.1	4.8
2	5	4 4	4.1
3	10	6.2	6.4
4	10	7.9	9.4

Table 2.—Activation Free Energy as Calculated From
Rate Process Theory for Selected Relaxation Times

Relaxation time, sec	10^2	10^3	10^4	10^5	10^6
Activation free energy, kcal/mole	20.1	21.5	22.9	24.25	25.6

DISCUSSION AND CONCLUSION

During the recovery process the boundary plates were held rigidly in their final positions so that no work was performed by internal forces during this stage. Nevertheless, the state of the system underwent a spontaneous change, and this was interpreted as a gradual re-establishing of bonds that had been displaced by shear. If we call such an event a *transition*, equation (1) represents the number of transitions per second *with no stress acting*. The transition frequency is determined by the temperature and by the activation free energy, i.e. the amount of free energy which must be received by a configuration before a transition can occur.

The experimental activation free energy of 21–23 kcal/mole determined

from the relaxation time can be put in perspective by referring to Bernal (1958) and Kittel (1962, p. 64). According to these authors, the ionic bond has an activation energy in the order of 10–20 kcal/mole, or more, which suggests that the bonds which are formed during recovery are Coulombic.

It is generally considered that a transition involves the making or breaking of a single bond. For example, in water (an associated liquid) the activation free energy for viscous flow is approximately that of a single hydrogen bond, although there are two hydrogen bonds linking each water molecule to its neighbours and many water molecules involved in a transition. Similarly, in the present case, it is assumed that the activation energy in the recovery process involves the formation of only a single bond during a transition even though the initial and final configurations involve two or more particles and many bonds. Hence, the values quoted above refer to the activation free energy *per mole of bonding sites*.

Langmuir (1938) measured the changing relaxation times of bentonite suspensions by a different method, using birefringence of the sheared suspension as a criterion for the rate of relaxation. The clay suspensions were more dilute, and the particles were somewhat smaller than in the suspensions reported upon here. The relaxation times varied from 3 sec to 80 hr, over the range of concentrations used. A 1.4% clay suspension gave a relaxation time of 220 sec at 0°C and 50 sec at 40°C, giving a calculated activation energy of 6.3 kcal/mole by Langmuir's method of calculation. Aside from the fact that Langmuir's experiments dealt with a different variable (the degree of anisotropy), his experimental activation energy values were for much more dilute suspensions, suggesting that he may have been dealing only with a threshold level of interaction between particles.

It is interesting to note that experimental activation energies of the same order of magnitude as those described herein have been measured by several workers in connection with temperature-dependent creep studies of clay systems (Muriama and Shibata, 1961; Mitchell, 1964; Mitchell and Campanella, 1963; Christensen and Wu, 1964; Campanella, 1965).

Low (1960), Kolaian and Low (1962), and Leonard and Low (1964) have interpreted the change of suction resulting from shear as being due to a change in the structure of the water. The results of the present experiment suggest that the change in configuration of aggregates of particles must also be considered, and perhaps that the latter may be the major source of the free energy change.

Particle interactions by Coulombic bonding conform to the current theories of the electrical double layer, and also take into account edge-to-face configurations. It is assumed that the recovery process may occur in a number of different ways, including translation and rotation of one particle with respect to another, bending and twisting of individual particles, etc. Each of these mechanisms involves Coulombic bonds. The magnitude of the experimental activation energy found for the recovery process suggests that the latter may be essentially a sequence of Coulombic interactions.

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