COMPACTION OF CLAY SEDIMENTS IN THE RANGE OF MOLECULAR PARTICLE DISTANCES

by

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ABSTRACT

The physical process of compaction of clay sediments and the inverse process of swelling can be discussed in terms of particle interaction forces. The swelling pressure in a given situation equals the net repulsive force per unit area between the particles. The net repulsive force is the resultant of various repulsive and attractive forces. Two stages of swelling or compaction can be distinguished, one in which the particles are relatively far apart, and a second in which they are separated by only a few monomolecular layers of water.

In the first stage the swelling pressure is primarily due to double-layer repulsion ("osmotic swelling"). The pressures range from a fraction of one atmosphere to several times ten atmospheres. These pressures are of particular interest for foundation engineering problems.

In the second stage the swelling pressures are dominated by the work of adsorption of the water layers on the clay surfaces. The pressures may reach several thousand atmospheres. Quantitative data on the swelling pressures in this range are derived from water vapor sorption isotherms combined with X-ray data on the *c*-spacing of expanding clays during dehydration.

It is concluded that overburden pressures in nature will seldom be high enough to remove all adsorbed water from between parallel grain surfaces.

INTRODUCTION

Because of the rather spectacular swelling phenomena observed when dry clays are contacted with water, there is a tendency to over-emphasize the importance of the direct interaction between clay particles and water. However, according to the data derived from water vapor adsorption isotherms of clays, the order of magnitude of the energy of hydration of clays per unit surface area is comparable to that of materials such as sand or quartz, but none of the spectacular swelling effects which are typical for clays are shown by such materials. The unusual swelling phenomena in clay–water systems can be attributed to the extreme anisodimensional shape of the clay particles. In the present study the swelling and compaction pressures of clay–water systems are interpreted by focusing attention on the mutual particle interaction forces of the suspended platy clay particles rather than on particle-to-water interaction energy. Nevertheless, the surface hydration energy of the

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https://doi.org/10.1346/CCMN.1962.0110116 Published online by Cambridge University Press

clay does enter the analysis to a certain extent, but only in the short-range particle interaction, which is emphasized in the present study. The forces dominating the longer-range particle interactions will be discussed briefly.

ACKNOWLEDGEMENT

The author wishes to acknowledge the careful determination of the adsorption–desorption isotherms and the *c*-spacing data by Mr. C. T. Deeds and Mr. W. K. Lumb. The water vapor adsorption equipment was designed by Mr. C. S. Brooks.

PARTICLE INTERACTION AND SWELLING PRESSURE

For simplicity we shall discuss first the causes of swelling and the definition of swelling pressure for the situation in which the platelike clay particles are oriented parallel to each other. Later we shall discuss the consequences of a nonparallel alignment of the particles.

Referring to Fig. 1, we consider a lower fixed clay plate and an upper movable clay plate parallel to, and a given distance from, the fixed plate. The two plates are immersed in water. The plates may be multilayer particles of a kaolinite or an illite, or a single unit layer of a montmorillonite.

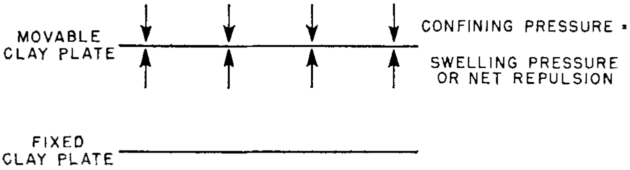

Figure 1.—Relation between confining pressure, swelling pressure, and net repulsion.

If at a given distance there is a tendency for the upper plate to move away from the lower plate, the system has a tendency to swell. Apparently, under these circumstances a net repulsive force operates between the plates. This net repulsive force per unit area is called the swelling pressure. In order to keep the upper plate at the given distance from the lower plate, a confining or compaction force must be applied to the top of the upper plate; this confining force is equal to the net repulsive force. Hence, the net repulsive pressure, or the swelling pressure, can be determined by measuring the confining pressure required to maintain the given particle distance, i.e. the particular clay/water ratio. This method for measuring swelling pressure is generally used in practice, particularly in foundation engineering laboratories.

The causes of swelling can be understood if the interparticle forces are analyzed. It appears that two ranges of particle distances, in which different interparticle forces play the dominant part, should be distinguished. In the region of molecular distances, i.e. up to about 10 Å, the dominant source of

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repulsion is the adsorption energy of water at the clay surfaces; the particles are pushed apart when the water molecules enter between the plates owing to their adsorption energy on the plate surfaces. In many systems, this hydration energy is large enough to overcome certain attraction forces between the plates.

At larger particle distances, at which the energy of water adsorption has decayed, the dominant cause of repulsion is the electrical double-layer repulsion.

LONG-RANGE PARTICLE INTERACTION AND "OSMOTIC SWELLING"

We shall discuss the longer-range particle interaction briefly before turning to the short-range repulsion, which is the main concern of the present communication.

At large separations between parallel clay plates, two contributions to the net interparticle force should be considered—a repulsive force due to the presence of diffuse electrical double layers on the charged clay plates, and the general van der Waals' attractive force between the plates.

As long as the double-layer repulsion is larger than the van der Waals' attraction, the system will have a tendency to swell. Since the double-layer repulsion may be discussed in terms of an osmotic repulsion due to the difference in cation concentrations between the plates and in the outside solution, the swelling in this range is often called "osmotic swelling".

The confining pressure required to maintain a given particle distance (or a given clay concentration) is equal to the double-layer repulsion minus the van der Waals' attraction. Often, the van der Waals' attraction is considered negligible with respect to the double-layer repulsion, and the confining pressure is considered a direct measure of the double-layer repulsion.

In principle, therefore, the determination of the confining pressure required to maintain a certain clay/water ratio would allow the evaluation of the double-layer repulsion at the particular distance between the clay particles prevailing at that clay/water ratio. For the computation of that distance one needs information about the average plate thickness.

The validity of this method depends on the validity of the assumption that the particles are in a parallel position throughout the system. It seems likely, however, that such an alignment is often not realized in practice. Because of the presence of positive charges on the edges and negative charges on the faces of the clay plates, there will be a tendency for a fraction of the particles to become associated edge-to-face, thus establishing cross links between the parallel plates. This cross linking has two consequences for the swelling phenomena. In the first place, the attractive force created by the cross linking particles between the parallel plates will limit the swelling due to the double-layer repulsion. In the second place, the confining pressure will be partly used as grain pressure in the rigid cross-linked framework of plates, and the

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fraction of the pressure directly acting against the repulsive pressure between parallel plates will be unknown.

For a further analysis of this problem the reader is referred to the work of Norrish (1954), Norrish and Rausell-Colom (1962), and van Olphen (1962).

In the range of particle distances described above, the volume changes of the system are considerable, and the swelling pressures amount to a few tenths of one atmosphere to several times ten atmospheres. This range of volume changes and pressures is of concern to the foundation engineer and to the sedimentary geologist in connection with the early stages of compaction of sediments.

SHORT-RANGE PARTICLE INTERACTION

The swelling behavior of clay–water systems in the range of particle separations below about 10 Å is of interest in sedimentary geology in studies of the compaction of sediments at large overburden pressures. As we shall show, extremely high differential pressures are expected to be required for the removal of the last few layers of water from between the plates. We are dealing with volume changes of at most 50 per cent for the case of the removal of the last four monolayers of water from between the unit layers of a montmorillonite clay. These volume changes will be proportionately less for the removal of water from between the grains of multilayer particles of clays such as kaolinites and illites.

Again, the swelling pressure or the confining pressure at a given plate distance will be equal to the net repulsive pressure between the plates.

In a previous paper (van Olphen, 1954) we have analyzed the forces which may be expected to contribute to the net repulsive force between the plates. These are the van der Waals attraction between the plates, the electrostatic interaction between the negatively charged plates and the counter ions, and the hydration repulsion due to the adsorption energy of water at the clay surface. It has been shown that usually the hydration energy is the dominating factor in the net interaction energy, but it should be emphasized that it is not the only operating force between the plates. We shall later return to the separate contributing forces of the net energy of interaction, but we shall discuss now the net effect only. Since the montmorillonite–water system lends itself better to a quantitative evaluation, we shall deal with the removal of water from this system by compaction, but the results will be of general validity for the removal of adsorbed water from between the surfaces of parallel flakes of nonexpanding clays.

PREDICTION OF COMPACTION PRESSURES FOR REMOVAL OF ADSORBED WATER

In the quoted paper (van Olphen, 1954) we have shown that the net work done to remove successive adsorbed water layers from a hydrated expanding clay immersed in water can be computed from the water vapor desorption

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isotherm of that clay. Simultaneously, the change of the basal spacing of the clay which accompanies the loss of each monolayer of water can be measured by X-ray diffraction. Hence, the force per unit area of the unit layer required to squeeze out each monolayer of water can be found by dividing the net work involved by the change in distance between the unit layers.

We have evaluated the work of removal of water layers from between the unit layers of various bentonitic clays for which desorption isotherms were reported in the literature. From these data a general idea about the order of magnitude of the required compaction pressures for the removal of successive adsorbed layers of water can be obtained. For example, for bentonite clay in the calcium form, the work of removal of the fourth, third, second, and last monolayer of hydration water is of the order of 5, 32, 65 and 140 ergs/cm^2, respectively. Since the unit layers move a distance of about 2.6 Å for every monolayer of water removed, the required pressures are found to be

$$\frac{140}{2.6 \times 10^{-8}} = 5.4 \times 10^9 \text{ dynes/cm}^2 \approx 5400 \text{ atm} \approx 79{,}000 \text{ psi}$$

for the last monolayer; for the next to last monolayer the required pressure is ≈ 2500 atm, or $\approx 37{,}000$ psi; and the pressure is less for the third and fourth monolayers, for which the binding energy with the clay surface appears to decrease rapidly.

These estimates show that considerable pressures will be needed to compact a clay sediment to the extent that the last adsorbed monolayers are desorbed and squeezed out.

In an analogous way one can estimate the lifting power of dry clays when they become hydrated by manipulation of the water vapor *adsorption* isotherms. The hydration pressures developed are estimated to be of the same order of magnitude as the compaction pressures evaluated above.

The above estimates have an approximative character. In the first place, they are made on the basis of literature data which were not detailed enough to obtain more precise results, particularly at low relative pressures, where the observations are insufficient for a good evaluation of the work of removal of the last monolayer of water. Moreover, in the dehydration of most bentonites, the successive dehydration steps are not clearly distinguishable in the desorption isotherms and in the X-ray diffraction patterns. Therefore, we have chosen a more suitable system for our further studies, in which we have been able to make more accurate predictions of compaction pressures. This system also appeared to be amenable to an experimental check of our predictions.

PREDICTION OF COMPACTION BEHAVIOR OF A VERMICULITE CLAY

For a more detailed study of the removal of interlayer water by compression we have chosen a vermiculite clay. This clay, from the Llano location in Texas, when converted from the natural magnesium form into the sodium

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form by ion exchange, appeared to be a very suitable object of study. The hydration of this clay occurs in two distinct stages, at which either one or two monolayers of water are present between the unit layers. For each stage of hydration, sharp and well-ordered X-ray patterns are observed. The basal spacings of the two hydrates are 11.8 Å and 14.8 Å, whereas the dry clay has a spacing of 9.8 Å. The two hydrates have well-defined stability regions, each covering a considerable range of equilibrium relative water vapor pressures, as shown by two plateaux in the water vapor adsorption and desorption isotherms.

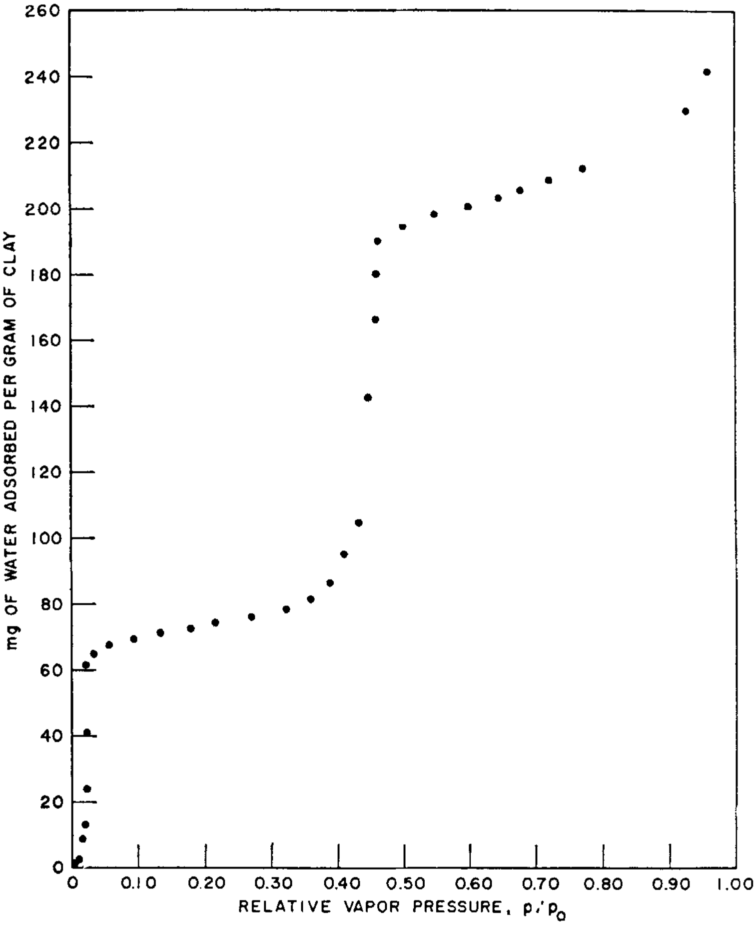

FIGURE 2.—Water vapor desorption isotherm of sodium Llano vermiculite at 25°C.

The isotherms were measured in great detail, particularly at low vapor pressures. Figure 2 shows the desorption branch of the water vapor sorption

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isotherm of sodium Llano vermiculite at 25°C.* The isotherm is rather exceptional in that it shows the two discrete hydration steps so clearly. Both parts of the isotherm have the characteristic shape of Langmuir isotherms. The monolayer coverage is best obtained from a Langmuir plot rather than from a BET plot. The monolayer coverage amounts to 74 mg of water per gram of clay.

A future publication will present a more detailed analysis of the energetics of water vapor adsorption on the vermiculite clay on the basis of the isotherm data combined with calorimetric data.

The work of removal of adsorbed water from a clay immersed in water can be computed from

$$V_R = \frac{RT}{18{,}000\ \Sigma}\left[\int_p^{p_0} \frac{n}{p}\,\mathrm{d}p + n \ln \frac{p}{p_0}\right],$$

in which V_R is the repulsive energy between the unit layers in ergs per square centimeter, R is the gas constant, T is the absolute temperature, Σ is the total number of opposite square centimeters of unit layer surface per gram, i.e. practically half the total unit layer surface area per gram, and n is the amount of water present on the clay in milligrams per gram of clay at the water vapor pressure p. The saturated vapor pressure is p_0, and the factor 18,000 converts the molar gas constant to ergs per °C per mg H_2O. The work of removal of one water layer is found from the change in the value of V_R in the corresponding range of values of n.

From a plot of n/p versus p, the integral term is evaluated graphically. In Fig. 3 the computed values of V_R are plotted as a function of the relative vapor pressure p/p_0 (curve 1) and of the amount of water on the clay, n (curve 2). The latter curve shows two straightline portions, relating to the successive removal of the two water layers, which intersect at the point of monolayer coverage. Apparently, the work of removal of a unit weight of water per unit area is a constant for either water layer.

The total work of removal of the second layer amounts to 35 ergs/cm^2, and that of the last layer amounts to 105 ergs/cm^2. During removal of the second layer, the unit layers approach each other over a distance of 14.8 Å–11.8 Å, or 3.0 Å. They travel a distance of 11.8 Å–9.8 Å, or 2.0 Å, when the last layer of water is squeezed out. Hence, the required compaction pressures for dehydration are 1.17×10^9 dynes/cm^2 for the second layer and 5.25×10^9 dynes/cm^2 for the last layer, or 1160 atm and 5200 atm, or 17,000 psi and 76,000 psi, respectively. Apparently, the second layer is comparatively weakly held by the clay, but the last layer is strongly adsorbed, and considerably higher compaction pressures are needed to remove this layer than those required for removal of the second layer.

The conditions for the removal of successive water layers can be expected to be less stringent at higher temperatures. In order to obtain an idea of the

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* The reference weight of the sample was obtained by drying to constant weight at less than 10^{-4} mm pressure at 50°C for three days.

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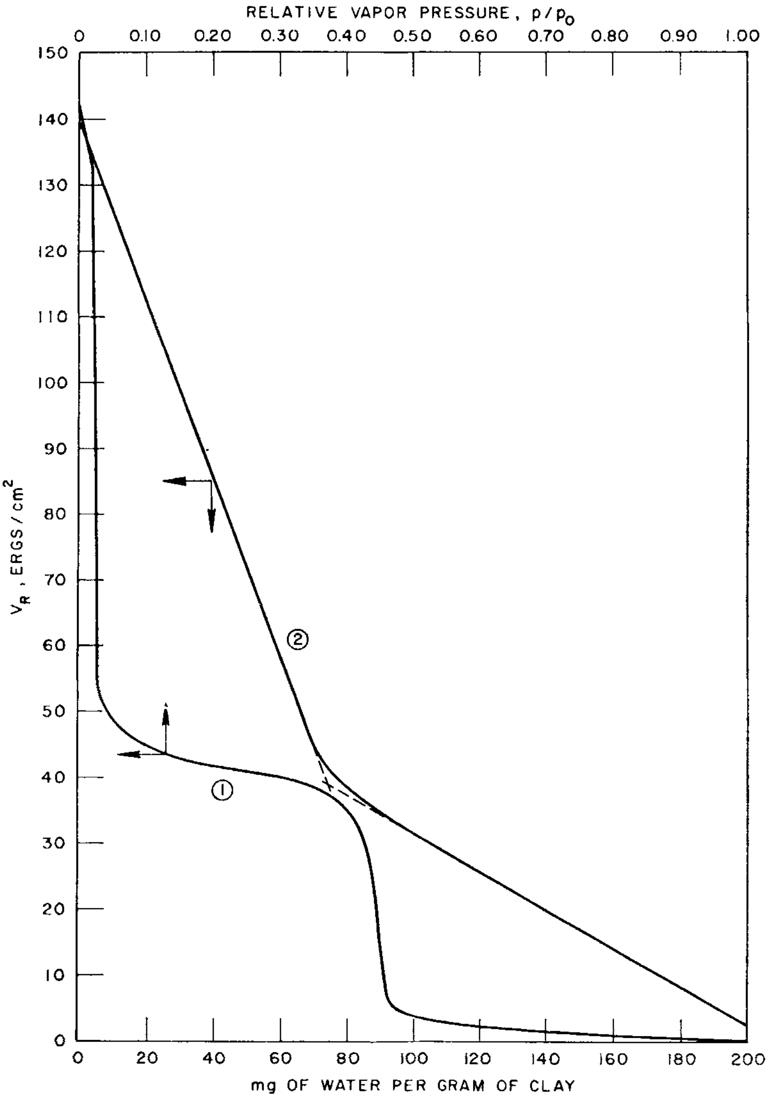

FIGURE 3.—V_R as a function of relative pressure (curve 1) and of water content (curve 2) for sodium Llano vermiculite, at 25°C.

effect of temperature, we have also measured the isotherms at 50°C for the same clay. Evaluation of the data in terms of the required pressures for dehydration gave the following results: The work of removal of the second and last monolayers of water at 50°C is 20 ergs/cm^2 and 90 ergs/cm^2, respectively.

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Hence, the required compaction pressures amount to 0.667×10^9 dynes/cm^2 and 4.5×10^9 dynes/cm^2, or 660 atm and 4450 atm, or 9650 psi and 65,300 psi, respectively.

EXPERIMENTAL CHECK

We have suggested checking these predictions experimentally by subjecting a hydrate of sodium Llano vermiculite to a differential pressure and simultaneously determining the basal spacing of the clay. An appropriate attachment for the X-ray diffraction equipment was developed by Steinfink and Gebhart (1962). A clay flake is loaded between a piston and a supporting platen. Squeezed-out water is allowed to escape sideways from between the unit layers. Evaporation is prevented by maintaining saturated water vapor pressure around the sample. The assembly is mounted in the X-ray diffraction apparatus in such a way that a pattern can be obtained of the specimen between the piston and the platen, which are both made of beryllium.

In agreement with the predictions, Steinfink and Gebhart found that the second layer of water in the sodium Llano vermiculite is gradually removed at loads in the range of 20,000–30,000 psi. In their paper an experiment is described in which the pressure on the specimen was 30,000 psi. The diffraction peak which is characteristic of the fully hydrated clay (14.8 Å) gradually diminishes, and a peak belonging to the monohydrate (11.8 Å) appears and grows in intensity.

Unfortunately, no check of the anticipated pressure for removal of the last layer of water could be performed, since the maximum operating pressure of the apparatus was about 30,000 psi.

One cannot expect high degree of accuracy in this type of experiment, since it is difficult to analyze the magnitude of the pressures exerted on the water layers. Perfect parallelism of the clay plates is probably not realized in the specimen; thus, grain pressures will be established, and only part of the applied pressure will be exercised on the fluid between parallel plates. Nevertheless, it is gratifying that at least the order of magnitude of the pressure required for removal of the second layer agrees with the prediction. Also the fact that the maximum pressure which could be obtained in the apparatus was insufficient to remove the last layer of water is in accord with the prediction.

CONCLUSIONS

According to adsorption isotherms for various kinds of clays, as well as for quartz, the energies of adsorption of water on these materials do not vary widely; therefore, removal of adsorbed water from between the surfaces of clay particles in general, as well as of quartz particles, will generally require extremely high compaction pressures—higher than those usually encountered in nature. Therefore, one can expect that complete removal of adsorbed

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water will seldom occur at the overburden pressures established in nature. However, the release of adsorbed water will be facilitated by an increase of temperature. In order to establish the effect of temperatures which may be encountered in nature, adsorption isotherms should be obtained at these temperatures. In addition, if the dehydration of the clay was accompanied by a volume change of the entire system, the effect of the over-all pressure level at great depths should be considered. Such volume changes probably do not occur for bentonite–water systems, but a volume change has been observed for the vermiculite–water system (Deeds and van Olphen, 1961).

Returning to the breakdown of the net repulsive force into three contributing forces, attention is drawn to the possibility that the hydration repulsion may be surpassed by a large electrostatic attraction force between the layers. This situation may occur when potassium ions are present between the layers. For example, when the sodium ions in sodium vermiculite are exchanged for potassium ions, the interlayer water is expelled spontaneously and the lattice "collapses" without any external compaction force. Although this is an extreme example, the increased tendency to collapse because of the substitution of interlayer cations by potassium ions is well known. Hence, in nature, the dehydration of clay sediments because of the substitution of exchange ions by potassium ions, whenever available, may cause the expulsion of water of hydration at compaction pressures considerably smaller than those anticipated for clays in different ion forms.

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