

## NOTE ON THE HYGROSCOPICITY OF CLAY AND THE QUANTITY OF WATER ADSORBED PER SURFACE-UNIT.

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As is well known, specimens of soil which have been exposed to the air until to all appearance quite dry, still contain a quantity of water, the so-called *hygroscopic* water. If the soil in question is of a coarse nature, as, for example, sand or silt, this amount of water is relatively small, while in the case of fine-grained clays it can amount to as much as 20 per cent. or more.

But the amount of hygroscopically-bound water is, of course, not solely dependent on the nature of the soil in question, but also on the greater or less saturation of the atmosphere with water vapour; that is, on the vapour pressure of the water in the air.

Curiously enough, there are for soils hardly any published researches on how the amount of this hygroscopic or adsorbed water (after equilibrium is reached) varies with changing pressure of water vapour in the atmosphere in which the research is conducted, while, in the domain of colloid chemistry, in the case of gels, this has shown itself to be an excellent method for characterising these in order to determine their internal structure.

I have therefore begun a research of this nature, conducted in such a way that the soil samples—up to the present they have been chiefly clays—were simply allowed to lie in a large desiccator containing a sulphuric acid-water mixture, the vapour pressure of which was taken by Regnault's<sup>1</sup> measurements. The weight was determined from time to time, and after about a month was found to be constant, showing that equilibrium had been attained between the adsorbed water and vapour pressure of the water in the atmosphere of the experiment. Thereupon the desiccator was filled with more concentrated acid, the clay gave off more water, and so forth.

If we plot on a curve as abscissæ the retained amounts of water (as percentage of the *dry* soil) and as ordinates the corresponding pressures of water vapour, we obtain for each clay a characteristic curve, of which some are given in Fig. 1.

It is clear that the coarser the clays are, the less water is held, and the closer the curves approach the axis of ordinates: while the stiff, strongly plastic clays give curves lying closer to the axis of abscissæ.

While the curves for nearly all clays are concave to the axis of abscissæ, it is remarkable that the curve for Egyptian Nile clay from Korashin lies almost in a straight line from 0 to 15 per cent. of water, and then gives a sharp bend.

While such *complete* curves giving the relation between adsorbed water and the vapour pressure are up to the present known only for a few kinds of soil, the amount of water retained over 10 per cent.  $\text{H}_2\text{SO}_4$  (corresponding to about 14.4 mm. at 18°) has, under the name of "hygroscopicity,"

<sup>1</sup>Regnault, *Ann. de Chim. et de Phys.* (3) 15, 179 (1845).

played a certain rôle in the study of soil since, according to a theory laid down by H. Rodewald,<sup>1</sup> the surfaces of the particles at this pressure of water vapour would be covered with a layer of water of one molecule thickness only, and E. A. Mitscherlich<sup>2</sup> calculated from this the total surface area of 1 gm. of the soil in question.

It has been pointed out many times that the whole of this theory is of a highly doubtful character.<sup>3</sup>

It is only necessary to proceed in the opposite direction and calculate from the surface area, which Mitscherlich calculated from the hygroscopicity, the average size of the particles, to find that one comes to such impossible results as that particles in a tertiary quartz sand should have a diameter of less than 1  $\mu$ , and that a stiff clay from Java should consist of particles of the dimensions of 1  $\mu\mu$ : that is, that their suspension would, in the ultra-microscope, be amicroscopic.

It is therefore of interest that one can, by my method of studying the rate of sedimentation in a clay slime, and its variations during the time of

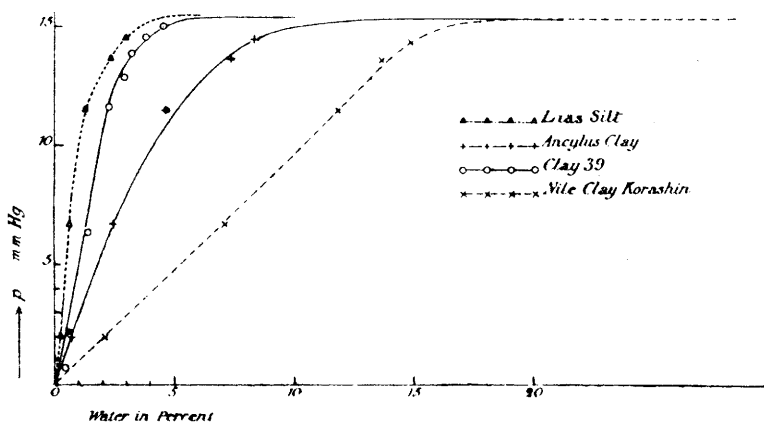


Fig. 1

sedimentation, obtain a measure of, at least, the order of magnitude of the total surface area the particles represent on their fall through the liquid.

If all the particles were spherical and we knew their distribution over the different ranges of size, that is, a function  $F(r)$  of such a nature that

$F(r)dr$  gives the percentage amount in the interval  $r$  to  $r + dr$  and the function  $N(r)$  is of such a nature that

$N(r)dr$  gives the number of particles in the same interval, we then have

$$F(r)dr = N(r)dr \cdot \frac{4}{3}\pi r^3 \sigma, \text{ where } \sigma = \text{the specific gravity of the particles,}$$

$$\text{or} \quad N(r) = \frac{F(r)}{\frac{4}{3}\pi r^3 \sigma} \quad (1)$$

<sup>1</sup> Rodewald, *Zeitschr. f. Physik. Chem.*, **24**, 218 (1897); **33**, 597 (1900); *Landw. Versuchsstationen*, **59**, 434 (1904); *Landw. Jahrbücher*, **31**, 675 (1902).

<sup>2</sup> Mitscherlich, *Bodenkunde*, 1 Aufl. (Berlin, 1905), 58 u.f.; 2 Aufl. (Berlin, 1913), 60 u.f.

<sup>3</sup> P. Vageler, *Fühlings Landw. Zeit.*, **61**, 77 (1912); P. Ehrenberg, *Fühlings Landw. Zeit.*, **63**, 725 (1914); **64**, 233 (1915).

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$N(r)dr$  gives the number of particles in the interval  $r$  to  $r + dr$ . If the interval is small we may regard the particles as of equal size and the *surface area* of each =  $4\pi r^2$ .

The combined surface areas of the particles in this interval of radius become therefore

$$N(r)dr \cdot 4\pi r^2 = \frac{F(r)}{\frac{4}{3}\pi r^3 \sigma} dr \cdot 4\pi r^2 = \frac{3F(r)}{r\sigma} dr \quad (2)$$

Finally, if  $O(r)$  is a function which gives the surface area as a function of the radius, so that

$$O(r)dr = \text{surface area in the interval of radius } r \text{ to } r + dr \text{ then clearly,} \\ O(r) = \frac{3F(r)}{r\sigma} \quad (3)$$

and it is possible by integration of  $O(r)$  from 0 to  $\infty$  to obtain the total surface area for the amount given by the distribution curve.

The experimental and theoretical methods of obtaining distribution curves from the rate of deposition have been indicated by me in another place.<sup>1</sup>

Here we meet, however, the difficulty that all the particles do not settle within the time of the experiment; that is, we get a distribution curve for only a part of the clay.

By tapping off this undeposited residue and determining its mean size of particle, I have endeavoured to obtain the total area for the undeposited portion, with a view to fixing the surface area for the whole of the clay.

It may be stated, as an example, that for the *Ancylus* clay in question—(the distribution curve for this clay is published in Paper III., Fig. 17)—the sedimented portion amounted to 69.1 per cent., varying from  $7\mu$  to  $0.17\mu$ .

The surface area of this 69.1 gm., that is, the function  $0.17 \int^7 O(r)dr$  amounted to  $1.62 \cdot 10^6$  sq. cm.

The mean size of particle in the residue was  $100\mu\mu = 1 \cdot 10^{-5}$  cm. The surface area of each particle was therefore  $4\pi \cdot 10^{-10}$  sq. cm.

For calculation of the total number of particles  $N$  the following equation applies:—

$$N \cdot \frac{4}{3}\pi(1 \cdot 10^{-5})^3 \sigma = 30.9 \\ N = \frac{30.9 \times 3}{4\pi\sigma} \cdot 10^{15}$$

and the surface area of all the undeposited particles

$$= 4 \cdot \pi \cdot 10^{-10} \cdot N = \frac{4\pi \cdot 30.9 \cdot 3}{4\pi\sigma} \cdot 10^5.$$

If the specific gravity  $\sigma$  is taken at 2.7, we obtain the result:—  
 for the undeposited portion  $3.43 \cdot 10^6$  sq. cm.  
 and for the deposited portion  $\frac{1.62 \cdot 10^6 \text{ sq. cm.}}{5.05 \cdot 10^6}$   
 thus for the whole 100 gm. of clay  $5.05 \cdot 10^6$   
 or 5.05 sq. m. per 1 gm.

In this way I obtained for 1 gm. of the Lias silt 1.78 sq. m. and for the clay 39, 1.62 sq. m.

<sup>1</sup> See my third paper on the "Clays as Dispersoids" and also "Koll, Zeitschr." 1917, 18, 33 (1916), 26, 100 (1920).

With the Nile clay disturbances unfortunately occurred in the registration so that I was not able to calculate the surface area.

If we now express the water content in gr. per sq. m., instead of in per cent. per unit weight, we arrive at the curves given in Fig. 2.

It is clearly seen that the curves do not coincide as one might expect

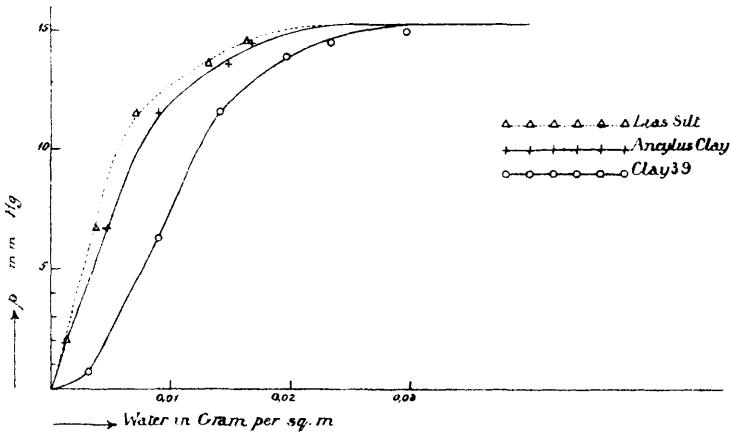


Fig: 2

if each surface unit absorbed the same amount of water independent of dispersity and of chemical nature.

Furthermore, even the sequence of the curves for water per unit surface, and those for water per unit weight, is not the same, so that a clay of higher "hygroscopicity" may have a smaller surface development than a clay of smaller hygroscopicity.

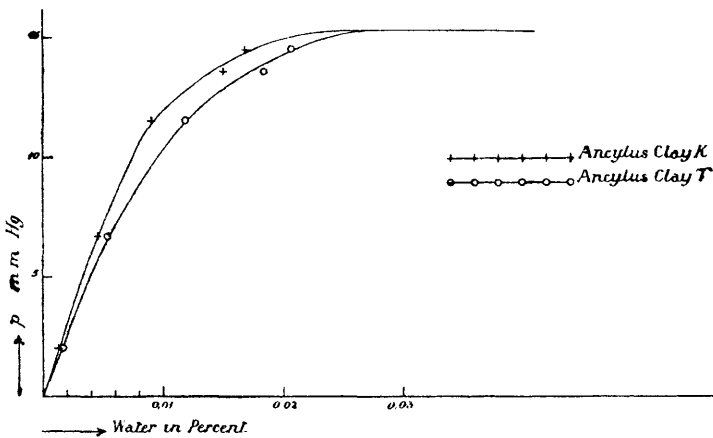


Fig: 3

It is, therefore, clear that calculation backwards from hygroscopicity to surface development of a soil is fallacious, the hygroscopicity being obviously dependent not only on surface development but also on the chemical nature and constitution of the clay.

Only when clays of closely related nature are considered, as *e.g.* layers

of varying thickness and dispersity of the stratified Yoldia clay, the curves for the water retention referred to the weight and to the surface coincide as is shown by the two diagrams in Figs. 3 and 4.

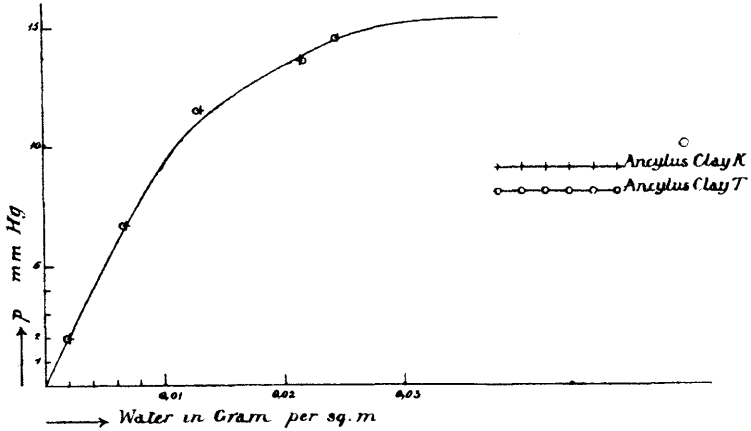


Fig. 4

Fig. 3 represents the water in per cent. by weight of two specimens with a surface development of  $3.4 \text{ m}^2$  and  $4.2 \text{ m}^2$  per gram weight, while Fig. 4 shows the water in grams absorbed per surface unit at varying pressures.