INTERNATIONAL SOCIETY FOR SOIL MECHANICS AND GEOTECHNICAL ENGINEERING

WATER SORPTION TEST FOR PARTICLE INTERACTION ESTIMATE

SORPTION DE L'EAU POUR L'ESTIMATION DES INTERACTIONS DES PARTICULES

ОПРЕДЕЛЕНИЕ СОРБЦИОННЫХ СВОЙСТВ ДЛЯ ОЦЕНКИ ВЗАИМОДЕЙСТВИЯ ЧАСТИЦ

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SYNOPSIS. From water sorption test the specific surface and mineral phase water in monomineral and natural clays are determined. From these values the long-range interparticle forces are calculated for Z.M. bentonite obtaining results comparable to the measured cohesion. There is proposed a complete method of clay mineral, montmorillonite, kaolinite, illite, organic matter content and CEC determination for engineering purposes.

INTRODUCTION

The accumulating knowledge in clay physics must result in new methods of clay physical parameters measurement, which would reflect definite physical properties of the investigated soils. It seems that for engineering purposes most interesting physical parameters are: the clay external specific surface, $\bar{S}$, and mineral phase water, i.e. water sorbed on the particle external surface and in the internal space /W_a, if determined at 110°C, W_m, if determined at 200°C/. From these two values the interparticle distance, 2d, in saturated clays as the function of water content may be estimated as:

$$d = \frac{W - W_a}{\bar{S}\rho_{H_2O}} \qquad (1)$$

which is the most important parameter in the long-range particle interaction calculation /here W is the water content in g H_2O/100 g clay, $\rho_{H_2O} = 1.0$ g/cm^3 is the free liquid water density/. The evaluation of W_a and $\bar{S}$ is the main subject of this paper.

Previous studies indicate that the diffuse layer interaction p_R and dispertion interaction p_A /van der Waals attraction/ are the two most important long-range interactions /internal stresses/ in clay - water system /Paszyc-Stępkowska, 1966, Stępkowska-Paszyc, 1967, Stępkowska, 1970/.

The diffuse layer interaction may be calculated from the generally known formula /Bolt and Miller, 1955/:

$$p_R = 2\ n\ k\ T\ \left(\cosh Y_d - 1\right) \qquad (2)$$

where n is the ion concentration as remote from the particle surface that the electric potential is zero (in ions/cm^3), k = 1.38×10^{-16} ergs/ion °K, T is the temperature in °K, Y_d is the dimensionless parameter of the electric potential in the middle between two parallel plates separated by the distance of 2 d.

$$Y_d = 2 \ln \frac{\pi}{\Delta}\ ; \quad \Delta = \mathcal{H}\left(d + x_o\right);$$

$$= \sqrt{\frac{8\ n\ e^2\ Z^2}{\varepsilon(d)\ k\ T}}\ ; \quad x_o = \frac{4\ Z\ c_o\ S}{\mathcal{H}^2\ \mathrm{CEC}}$$

where e = 4.803×10^{-10} e.s.u. is the elementary charge. Z is the exchangeable ion valency, d is the dielectric constant of water which is a function of the interparticle distance, c_o is the salt concentration in mol/l, S is the total specific surface in cm^2/g clay, CEC is the cation exange capacity in meq/g clay.

The dispersion interaction may be calculated from the formula:

$$p_A = -\frac{6.29\ C}{^{-}\quad d}\ \frac{1}{d^3} + \frac{1}{d\ +\qquad ^3} - \frac{2}{d+\quad /2\ ^3}\qquad 3$$

where C is a constant calculated for montmorillonite as 4.02×10^{-14} ergs, ^{-}d is the effective dielectric constant in the clay - water system, is the particle thickness /for detailed calculations see Stępkowska, 1970/. Both p_R and p_A may be derived from the interaction potential energy.

The knowledge of long-range particle interactions might be a valuable tool for the stability analysis and shear strength evaluation. Therefore much effort was given to their evaluation in monomineral clays /first step/ and in natural soils as the final solution. The possibility of interparticle distance determination in natural soils seemed to be the most difficut stage. The method proposed below is possibly the positive solution. Its mineralogical justification was presented to the 1972 International Clay Conference /Madrid/ and is to be published elsewhere /Stępkowska, 1973/.

The method consists in the water sorption measurement at relative water vapour pressure $p/p_o = 0.5$ $W_{.\ ..;0,5}$; 0.95 $W_{.\ ..;0,95}$; 1.0 $W_{.\ ..;1,0}$ of the following samples:

1/ fraction finer than 2 u homoionized a to Mg $W_{.\ Mg;...}$; b to K $W_{.\ K;...}$;

2/ fraction finer than 0.1 mm $W_{.\ 0.1\,mm;...}$

3/ fraction coarser than 0.1 mm $W_{.\ 0.1\,mm;...}$

Sorbed water content is determined either at 110°C $W_{a\ ..;...}$ or at 200°C $W_{m\ ..;...}$. The clay external specific surface $\bar{S}$ is determined from $W_{a\ K;0.5}$ assuming on the external surface a bimolecular water layer of the density 1.27 g/cm^3. Internal specific surface is determined from $W_{m\ Mg;0.5}$ - - $W_{a\ K;0.5}$ assuming a monomolecular intersheet water layer of the density 1.46 g/cm^3. Total specific surface S is calculated either from $S = S-\bar{S} + \bar{S}$ or from $W_{m\ Mg;0.95}$ assuming a bimolecular water layer of the density 1.27 g/cm^3. Mineral phase water W_a /Eq. 1/ is determined from $W_{a\ Mg;0.95}$ 1.27 /polywater at $p/p_o = 0.95$, normal water in wet state/. From the ratio of $S-\bar{S}$ to the theoretical value $790-\bar{S}$ m^2/g the montmorillonite content M including vermiculite is estimated. Clay mineral content C.M. in the given fraction is estimated from the ratio of water sorption of natural sample to that of Mg clay as measured at $p/p_o = 0.5$ 0,55/ C.M. = $W_{m\ 0.1mm;0.5}$ $W_{m\ Mg;0.5}$. CEC may be assessed from the external specific surface assuming 17 $Å^2$ per elementary lattice charge.

It is proposed to estimate roughly the organic matter content O.M. , which actually interferes in the determination, from the weight loss due to heating from 200°C to 400°C. Kaolinite content Kl including partly chlorite may be evaluated roughly from the weight loss G due to heating from 400°C to 800°C, assuming G = 4.5 % for montmorillonite and illite and G = 13.9 % for kaolinite. Illite may be determined from K_2O content assuming 6 % for illite.

The test may be performed by an intelligent technician, equipped by the detailed procedure descriptiom /Stępkowska, 1973/ and some practice. The equipment necessary is : centrifuge, desiccators flat ceramic crucibles, two drying ovens, combustion oven, analytical balance, agate mortar etc. It is advisable to send prepared samples for supplementary tests /derivatograph, diffractograph, chemical analysis for K_2O content, exchangeable cations/.

TEST AND CALCULATION RESULTS

Tests were performed on several clay samples. Results are presented elsewhere /Stępkowska, 1973/. Here the example of Z.M. bentonite will be discussed in detail and the values determined will be used for calculation of long-range particle interactions /internal stresses Eq. 1 and 2/:

The following water sorption values were obtained in g H_2O/g clay :

$$W_{a\ Mg;0.5} = 16.53 \pm 0.50 \qquad W_{a\ Mg;0.95} = 30.65 \pm 0.64$$

$$W_{m\ Mg;0.5} = 20.42 \pm 0.11 \qquad W_{m\ Mg:0.95} = 34.92 \pm 0.23$$

$$W_{a\ K;0.5} = 8.21 \pm 0.23 \qquad W_{a\ K:0.95} = 16.22 \pm 0.79$$

$$W_{m\ K;0.5} = 8.36 \pm 0.23 \qquad W_{m\ K;0.95} = 16.39 \pm 0.72$$

Mineral phase water W_a /Eq.1/ was determined from the water sorption of Mg - bentonite at $p/p_o = 0.95$ /samples with all the exchangeable cations except K indicated similar water sorption at this condition/.

$$W_a = \frac{W_{a\ Mg;0.95} \times 1.0\ g/cm^3}{1.27\ g/cm^3} = \frac{30.65 \times 1.0}{1.27}\ g\ H_2O/g\ clay = 24.13\ g\ H_2O/g\ clay$$

This value takes into account the bimolecular water layer on the external particle surface and water in the internal space, considering both as belonging to the mineral phase.

The external specific surface /Eq. 1/ was calculated from :

$$\bar{S} = \frac{W_{a\ K;0.5}}{2\ \varnothing_{H_2O}\ \ H_2O} = \frac{8.21}{7.0104} \times 100\ m^2/g = 117\ m^2/g$$

here $\varnothing_{H_2O} = 2.76$ Å, $H_2O = 1.27\ g/cm^3$. This value as determined from the first maximum on the differential heat of wetting curve, assuming a monomolecular water layer of the density 1.46 g/cm^3 was $\bar{S} = 114\ m^2/g$. The external flat specific surface as determined from X-ray diffraction measurement of the particle thickness was for natural bentonite $\bar{S} = 101\ m^2/g$ and ranged between 98 m^2/g for Al-bentonite and 137 m^2/g for K-bentonite.

Therefrom the CEC value was estimated:

$$CEC = \frac{\bar{S}}{17 \times 10^{-20} m^2/charge \times 6.025 \times 10^{20}\ charges/meq} = \frac{117}{102.4}\ meq/g = 1.14\ meq/g\ clay$$

CEC as determined by Ba - ion exchange and X - ray fluorescence analysis against kaolinite standard /Paszyc-Stępkowska and Nowacki, 1965/ was CEC = 1.31 meq/g clay, as determined by NH_4 - ion it was CEC = 1.08 meq/g clay. The sum of exchangeable cations was for natural bentonite 1.33 meq/g, it was for bentonite nearly homoionic to various exchangeable cations about 1.07 meq/g clay and for Ca- bentonite it was 1.21 meq/g clay

The internal specific surface was :

$$S - \bar{S} = \frac{W_{m\ Mg;0.5} - W_{a\ K;0.5}}{1/2\ \varnothing_{H_2O}\ \ H_2O} = \frac{20.42 - 8.21}{2.015} \times 100\ m^2/g\ clay = 606\ m^2/g\ clay$$

This results in total specific surface $S = /S-\bar{S}/ + \bar{S} = 723\ m^2/g$ clay. S.Andrei /INCECRC, Bucuresti/ determined the total specific surface of Z.M. bentonite from the heat of wetting as S = 660 m^2/g clay.

The montmorillonite sontent is :

$$M = \frac{S - \bar{S}}{790 - \bar{S}} = \frac{606}{790 - 117} \times 100\ \% = 89.9\ \%$$

Inserting W_a and $\bar{S}$ into the Equation 1 the relation between water content and interparticle distance may be found.

From Eq.2 diffuse layer interaction may be calculated, e.g. for bivalent /Z = 2/ Ca bentonite:

$$n = c_o N_o = 10^{-7}\ \mathrm{mol/cm^3} \times 6.025 \times 10^{23}$$

$$\mathrm{ions/mol} = 6.025 \times 10^{16}\ \mathrm{ions/cm^3}$$

where N_o is Avogadro number.

The dielectric constant as the function of interparticle distance is:

$$d = \frac{d - 2.76 \quad 80.36 + 2.76 \times 41.68}{d}$$

where 80.36 is the electrostatic dielectric constant and $\frac{80.36 + 3.0}{2} = 41.68$ is the average value between the static and optical dielectric constant assumed for the third layer of sorbed water molecules. This is a first approximation not considering the influence of exchangeable cations in the diffuse layer on the water dielectric constant.

From E_q.3 dispersion interaction may be calculated (Stepkowska, 1970).Here for short range interactions:

$$\bar{\mathcal{E}}(d) = \frac{d\,\mathcal{E}(\omega) + (\delta/2)\mathcal{E}}{d + \delta/2}$$ part, where assumed $\mathcal{E}(\omega) = 3.0$,

The particle thickness as determined diffractometrically is = 120.3 ± 2.5 A°, dielectric constant of the mineral phase $_{part}$ = 3.70. Here the C = 4.02×10^{-14} ergs differs from the value indicated in the above mentioned paper 4.32×10^{-14} ergs , where for sorbed water there was assumed $_{H_2O}$ = 1.27 g/cm³ both in submerged state and in water vapour atmosphere at $p/p_o = 0.95$.

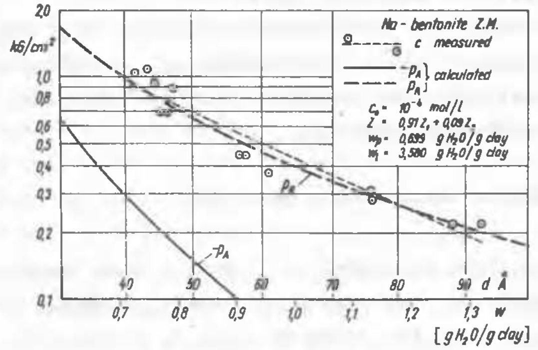

Fig. 1

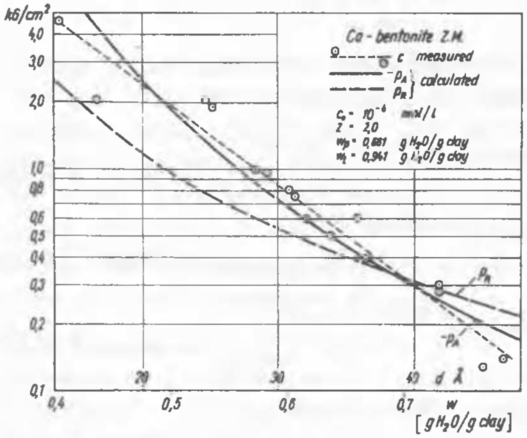

Fig. 2

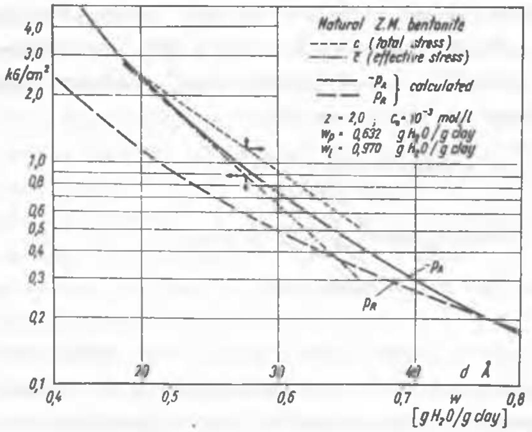

Fig. 3

COHESION MEASURED AND INTERNAL STRESSES CALCULATED /p_R and p_A/ AS THE FUNCTION OF WATER CONTENT.

Calculations of diffuse layer interaction p_R were performed also for Na bentonite Z.M. $Z=0.91\ Z_1 + 0.09\ Z_2$, where $Z_1 = 1$ and $Z_2 = 2$, as determined from the percentage content of Na and Ca - exchangeable cations .

In the Fig. 1 and 2 there are given calculation results for Na - and Ca - bentonite as compared to the results of cohesion c measurement /triaxial undrained quick test on remolded sample in terms of total stress/ these test results were published previously /Paszyc-Stępkpwska, 1960/. Here by the least square method the straight linear relation between log c and water content was determined as:

$$\log c = -\ 1.176\ w + 0.810;\quad r_{xy} = -\ 0.957 \text{ for Na-bentonite}$$

$$\log c = -\ 3.851\ w + 2.207;\quad r_{xy} = -\ 0.975 \text{ for Ca-bentonite}$$

here w is expressed in g H_2O/g clay.

The agreement between the calculated diffuse layer interaction p_R and the cohesion measured for Na-bentonite (Fig.1) is surprising. The cohesion of Ca-bentonite $w = w_p + 0.5\ \ w_1 - w_p\ = 0.80$ g H_2O/g clay is close to the dispersion interaction - p_A /Fig. 2/.

In the Fig. 3 there are given cohesion values /o in terms of total stress, $\bar{c}$ in terms of effective stress/ as measured by the triaxial test for natural Z.M. bentonite /static compaction $w = w_{opt}$, strain rate 2 %/hour, UU-test with pore pressure measurement, published Paszyc-Stępkowska, 1966/. Results are similar to those obteined for Ca-bentonite. The relation calculated by least square method is:

$$\log c = -\ 3.634\ w + 2.125;\quad r_{xy} = -\ 0.887 \text{ in terms of total stress}$$

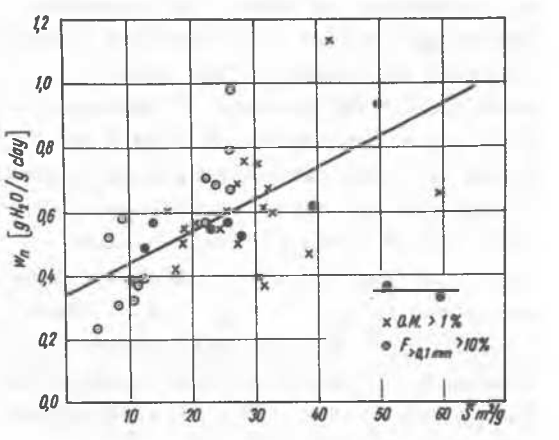

Fig.4. NATURAL w.c. AS THE FUNCTION OF EXTERNAL SPECIFIC SURFACE $\bar{S}$ /MARINE CLAY P.P/

$$\log c = -\ 4.763\ w + 2.636;\quad r_{xy} = -0.837 \text{ in terms of effective stress}$$

In the Fig.4 there is given the relation between the natural water content and the external specific surface as determined for the marine clay P.P.The relation calculated by the least square method for samples containing less than 10% of the coarse fraction 0.1 mm and less than 1% O.M.is $\bar{S}$ in m^2/g :

$$W_n = 1.01\ \bar{S} + 33.8 \quad g\ H_2O\ \ 100\ g\ clay \qquad r_{xy} = 0.856$$

The correlation between $\bar{S}$ and the liquid limit is much worse, $r_{xy} = 0.646$ and still worse is the correlation between $\bar{S}$ and plastic limit $r_{xy} = 0.446$.

Between the plastic limit and the mineral phase water of the natural soil $W_{m\ nat}$;0.95 the correlation was found:

$$W_p = 1.41\ W_m + 19.8 \quad g\ H_2O/100\ g\ clay \qquad r_{xy} = 0.624$$

CONCLUSIONS

The results presented indicate that the method proposed enables of the measurement of clay parameters necessary to calculate the long-range particle interactions /internal stresses/ in saturated and nearly saturated clays. The valency of exchangeable cation and salt concentration should be determined by other methods; usually bivalent Ca-ion prevails and salt concentration is about 10^{-4} to 10^{-3} mol/l. The cohesion measured is of the order of calculated interactions, close to p_R if p_R p_A ; close to - p_A if p_A p_R. The explanation of the mechanism of the shearing process needs a further study of the model of interaction of long-range interparticle pressures /internal stresses/ and the externally applied load. This problem is being studied now; the further step demands the consideration of unsaturated clays. It should be mentioned that in clays containing nonmontmorillonitic clay minerals /e.g. marine clay P.P/ the interparticle distance seems to be the function of some „dead water". The determination of this second term in the numerator of Eq. 1 for natural clays is the subject of further study.

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