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PHYSICO-CHEMICAL PROPERTIES OF SOILS

HANS F. WINTERKORN
Princeton University

SUMMARY.

The paper points out first the importance of structure and constitution of soils which govern the effectiveness of compositional factors. Next, the ordinary soil - engineering properties are shown to be derived from more fundamental surface and interfacial relationships between solid components and soil moisture. This leads to a demonstration of the importance of physico-chemical phenomena in all types of soil stabilization, and to the conclusion that knowledge of physico-chemical soil phenomena is a "sine qua non" for the engineer engaged in soil stabilization and a good tonic for the devotee of soil mechanics and foundation engineering in general.

The civil engineer dealing with soil is usually interested in its properties as a system and only rarely in the properties of the component particles. This is true not only for undisturbed but also for disturbed subgrade soil and base material. Except for cohesionless materials, disturbance by engineering use never breaks a cohesive soil system into its primary components.

The scientist, follows the "divide et impera" technique. He separates the material under consideration into fractions of like or similar properties, studying the characteristics of these fractions and even of the individual components. He proceeds from higher to lower levels of structure and arrives finally at the atomic and electronic levels. The engineer appreciates these divings to the lower levels of structure only if they result in bringing forth something useful on the working level.

The physical chemist, to be of real assistance to the engineer, must be a generalist as well as a specialist; he must understand that material properties are functions of the constitution as well as of the composition of the material; he must realize that, as a result of this constitution, the properties of a system may be more or may be less than the sum of the properties of the components. If the physical chemist is not sufficiently versatile to move freely, as necessity requires, from one level of structure to another, then he is, at best, a help-meet and, at worst, a seducer to the engineer. Possessing this versatility, this "ingenium", he can be truly an engineer and a teacher of engineers.

Physical chemistry offers fundamental explanations for observed soil-mechanical properties and indicates rational methods for improving soil properties (soil stabilization).

Soil systems are normally composed of solid, liquid and gaseous phases. The composition and character of these phases vary from soil to soil and within the same soil often from season to season. Of greatest importance to the engineer are the soil-water relationships. Since water can react only with the surface of the soil solids, the specific surface (surface/volume) of a soil is important. One percent of clay in a sand contributes more than ninety percent of the total internal surface. This illustrates the importance of the clay content; it is, however, not the whole story. Depending upon its chemical composition and environmental factors, clay is normally not in a dispersed but in an aggregated condition. Therefore, in most soils the calculated internal surface of clay is a potential not

an actual one, also, the soil mechanical "weight" of the clay depends on whether and to what extent it is present as a film around the coarser particles or as a filler in the pore spaces between the sand grains. The structural location, and, therefore, the role which a clay plays, depends on its own surface-chemical character as well as on that of the coarser material. On one hand, 1% of clay or other mineral cementing material may make the difference between a loose sand and a sandstone. On the other hand, if there exists no affinity between the clay and the coarse material, i.e. if the clay serves only as a pore filler, then we may incorporate into a sand, possessing a compacted density of 100 lb/cu ft as much as 30% of a clay (on the basis of the weight of the sand), which may double its volume by swelling in water, without appreciably affecting soil stability in moist condition. It is because of this situation that highway soil classifications consider as granular materials those which contain up to 35% of fines passing the No. 200 sieve. The actual role of clay in a soil may and normally does range between the two extremes indicated.

The phenomena resulting from the interaction of the mineral surfaces and water depend on the properties of the water as well as on those of the minerals. The properties of the water are as complex as those of the minerals. 1), 2), 3). In accordance with its molecular weight and in analogy with similar compounds (H_2S , H_2S^e , H_2Te^e), water should be a gas at normal temperatures, but it is a liquid; furthermore, x-ray examination of this liquid reveals properties normally associated with solids. This behavior is a consequence of the dipole nature and architecture of the water molecule. A dipole is a molecule in which the action center of the positive charges does not coincide with that of the negative. Some dipole molecules have only one pole sufficiently exposed to be reactive with other molecules or ions, while the other pole is sterically protected. In the water molecule, both poles are relatively accessible, which permits the molecule to freely associate itself with other molecules of its own kind or with other positively or negatively charged components of matter. The dipole character of water and the fact that soil minerals possess electrically charged surfaces, makes the whole field of soil-water relationships a branch of applied electrostatics 4), 5), 6).

Different soil minerals possess different electric surface structures. Because of the importance of the electric surface pattern for the understanding of mineral-water relation-

TABLE I
Comparison of Consistency Properties of Clay
Fraction and Whole Soil.
 Plasticity Index

Lab. Symbol	Soil Series and Texture	Mechanical Analysis %				determined clay ² fraction	whole soil (a)	calculated whole soil		P.I. Ratios		% of organic matter in		Liquid Limit (d) whole soil	Liqud Limit (e) colloid
		sand	silt	1) clay	2) clay			(b) ³	(c) ⁴	(a)/(b)	(a)/(c)	soil	colloid (extracted)		
P	Stephenville loamy sand	77	12	11	7.4	30.4	2.0	2.2	3.3	0.9	0.6	1.0	13.6	19.0	76
B	Zaneis sandy clay	67	11	22	12.5	36.2	4.1	4.5	3.0	0.9	0.5	1.4	10.9	22.1	84.6
E	Durant sandy loam	50	32	18	7.3	28.8	4.2	2.1	5.2	2.0	0.8	2.5	34.0	22.5	70.9
L	Foard loam	55	28	17	6.5	28.2	5.6	1.8	4.8	3.1	1.2	1.5	22.8	23.0	71.0
U	River Wash silty clayloam	39	41	20	10.8	49.9	11.7	5.4	10.0	2.2	1.2	1.3	12.2	31.8	92.0
M	Zaneis clay loam	45	30	25	21.8	33.4	13.7	7.3	8.4	1.9	1.6	1.8	8.2	32.1	80.0
N	Miller silty clay	33	27	40	34.2	40.9	26.1	14.0	16.4	1.9	1.6	2.0	5.7	45.0	82.8
V	Vernon clay	34	21	45	27.2	47.1	31.1	12.8	21.2	2.4	1.5	3.0	11.2	53.5	91.8

- 1.) clay content from sedimentation curve
- 2.) -2- micron clay from exhaustive extraction (soil residue had P.I. = 0)
- 3.) P. I. of extracted clay X percentage of clay obtained by extraction
- 4.) P. I. of extracted clay X percentage of clay from sedimentation curve.

All the soils in the Table come from the State of Oklahoma; the colloidal fraction of these soils (except for soil M) were found by differential thermal analysis to consist of illite and organic matter; soil M appears to contain a small amount of Kaolinite in addition to illite and organic matter. From the thermal analysis it appears also, that soils E, L, P, and N possess a similar type of organic matter differing from that of the other soils by a relatively higher range of combustion temperature.

snips, the elucidation of clay crystal structure is of great value in theoretical soil physics. Hogentogler has shown that the plasticity index of mixtures of sand with diatoms, kaolin, and bentonite, respectively, equals the product of the clay mineral percentage and a proportionality constant. 7)

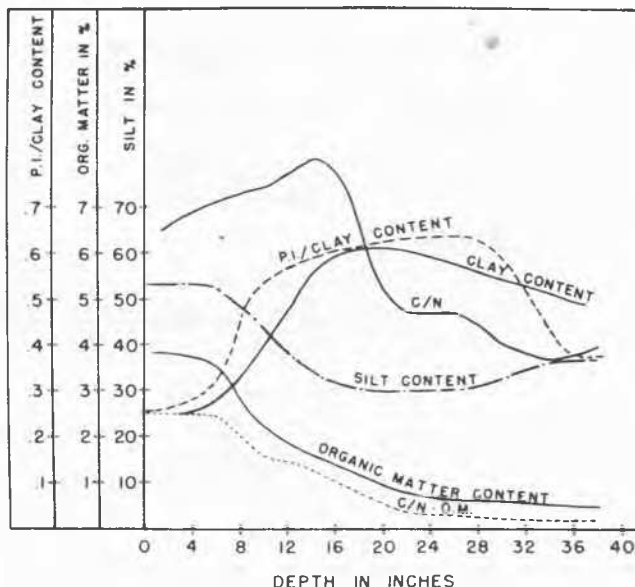
This relationship has been utilized also by clay mineralogists interested in foundry sands and ceramics. Some have even suggested that it is only necessary to know the amount and mineralogical character of the clay fraction in order to predict the behavior of a whole soil. This is unwarranted for a large number of reasons, only a few of which can be cited here.

The indicated relationship can exist only in artificial and structureless mixtures, but not in natural soils endowed with structure. Clay minerals in natural soils are not as clean as a scraped bone; rather, the mineral surface is normally in as close a relationship with adsorbed and syn-active organic matter as a bone in a living being is with cartilage and muscle tissue.

Opposite the indicated unwarranted simplification stands the complex reality as illustrated in Graph I and in Table I, respectively.

The tabulated data bring out an additional point, which is concerned with the problem of soil classification, and the discretion which must be employed in the practical use of any classification.

In the U.S. Engineers classification, organic silts and clays are separated from their inorganic counterparts by a line which



Factors influencing the plastic index

GRAPH 1

follows the equation:

$$P. I. = 0.73 (L. L. - 20)$$

If plotted, the data given in table I for the extracted colloids fall on the organic side

TABLE 2

Clay mineral - water relationships.(13)

Colloidal property	Type of H-colloid				
	Bentonite	Lufkin	Putnam	Susque-nanna	Cecil
Type of mineral	Montmorillonite	Montmorillonite Beidellite	Beidelite	Beidelite	Halloysite
SiO_2/R_2O_3 ratio...	5.0	3.8	3.2	2.3	1.3
Exchange capacity m.e. per 100 g	95.0	82.0	65.0	47.0	13.0
Hygroscopicity, % (30% H_2SO_4)	21.5	20.1	18.1	15.5	6.1
Heat of wetting cal/g		15.0	13.8	11.7	5.9
Swelling, cc./gm	2.2	1.18	0.81	0.57	0.05
Swelling Exchange Capacity	2.44	1.44	1.24	1.21	0.41
Hygroscopicity Exchange capacity	6.22	0.24	0.28	0.33	0.47
Swelling Hygroscopicity	10.23	5.87	4.47	4.87	0.91

TABLE 3.

The Effect of Exchangeable Cations on the Properties of Colloidal Clays.

Colloidal system	Colloidal property	Nature of cation					
		H	Li	Na	K	Ca	Ba
Putnam	Hygroscopicity						
	(a)	18.13	17.13	16.53	12.75	17.37	16.29
	(b)	44.76	56.12	49.22	31.12	40.91	41.95
	Heat of Wetting cal/g	13.6	12.0	12.0	9.5	15.0	13.9
	Swelling cc/g	0.81	4.97	4.02	0.50	0.91	0.85
	Hydration (c) cc/g	5.20	5.25	5.25	4.07	5.20	5.20
	Dispersity (d)	37.4	60.1	62.2	56.3	4.9	24.4
	Swelling cc/g	2.20	10.77	11.08	8.55	2.50	2.50
Wyoming Bentonite	Hydration (c) cc/g	35.0	28.4	24.1	21.3	24.2	34.0
	Dispersity (d)	34.0	37.8	35.2	35.7	31.2	31.9

- (a) % H₂O absorbed over 30% aqueous H₂SO₄ solution;
 (b) % H₂O absorbed over 3.3% aqueous H₂SO₄ solution;
 (c) calculated from viscosity data by means of the Einstein equation.
 (d) % particles smaller than 100 milli microns.

of the dividing line, while those for the whole soils fall on the inorganic side. Testing only the whole soils, there exists a serious danger that the organic matter in the soil be overlooked. For some applications, this may not be of great importance. For purposes of soil Stabilization, however, the "hidden" organic matter may make the difference between success or failure.

If the charge pattern on the surface of a solid soil constituent is ionic, it is matched by adsorbed ions of opposite charge. In the presence of water these adsorbed ions are partly dissociated into the surrounding water envelopes. These ions are exchangeable, i.e. they may be replaced by other ions.

If the mineral surface is predominantly negative, the counter-ions are positive or cations, and the soil possesses a cation-exchange capacity. Positively charged minerals possess an anion exchange capacity. If the electric field is of mixed character, then the system possesses both, cation and anion exchange capacity. Cation exchange capacity predominates in regions of temperate climate, anion exchange capacity predominates in soils developed under tropical weathering. The ion exchange capacity is usually expressed in milli-equivalents per 100 g of soil or clay. This exchange capacity is a property of any solid built up of ionic constituents; however, because clay contributes the largest relative amount of internal surface to a soil, practically all the exchange capacity of a normal soil is a function of the amount and type of its clay content.

With pure minerals, the exchange capacity can be related directly to the crystal structure. Minerals and especially their surfaces are rarely pure, however, in soils. For the same reason, the older characterization by means of the silica-sesquioxide ratio continues to be of practical importance in correlating clay-water relationships with chemical compositional factors. Furthermore, organic soil constituents contribute a large share of the exchange capacity of normal soils, and through this and other means influence soil-water relationships. Considering, also, the very close, almost symbiotic, physical relationship between organic and inorganic clay constituents existing in an actual soil, it becomes obvious, that exchange capacities of soils cannot be predicted from their mineralogical composition, but must be determined experimentally.

Table 2 illustrates relationships between water-affinity, base exchange capacity, silica-sesquioxide ratio, and type of clay mineral.

Table 3 illustrates the effect of the type of exchangeable ions on the water-affinity of Putnam clay and Wyoming bentonite.

Table 4 shows the effect of different exchange ions on whole Putnam soil.

Comparison of the data for Putnam clay in Table 3 and for the whole Putnam soil in Table 4 indicates clearly the modifying influence of the other soil fractions on the role played by the clay.

Materials added to soils for stabilization purposes will react physically or chemically with the surface of the soil solids. The type

TABLE 4. (14)

EFFECT OF EXCHANGE IONS ON ENGINEERING
PROPERTIES OF PUTNAM SOIL

Ion	Nat	H	Na	K	Mg	Ca	Al
<u>TEST</u>							
Lower liquid limit	64.5	56.4	88	52.8	56.3	61.9	60.2
Lower plastic limit....	23.5	24.8	25.4	27.7	25.4	27.0	26.3
Plastic index.....	41.0	31.6	62.6	25.1	30.9	34.9	33.9
Volume change F.M.E....	56.0	52.4	68.6	40.1	68.9	63.8	51.7
Shrinkage limit.....	17.9	16.3	11.8	19.4	12.	12.4	16.4
Shrinkage ratio.....	1.91	1.94	2.08	1.80	2.01	2.00	1.95
Field moisture equivalent.....	47.2	43.3	44.8	41.7	46.7	44.3	42.9
Specific gravity.....	2.708	2.663	2.661	2.675	2.645	2.680	2.721
Hygroscopic moisture...	5.79	5.32	4.20	4.60	4.38	5.76	6.69
Vacuum moisture equivalent.....	57.1	54.3	Water logged	53.7	58.7	58.9	55.1
<u>Mechanical Analysis</u>							
Per cent passing No.40	100	100	100	100	100	100	100
Per cent passing No.60	99.6	99.8	99.4	100	99.8	99.8	99.8
Per cent passing No.200	98.1	98.7	97.5	98.5	98.5	98.5	98.3
Silt (.05-.005mm).....	39.0	46.0	33.0	48.0	45.0	47.0	49.0
Clay (.005 mm).....	54.0	48.0	61.0	44.0	49.0	45.0	44.0
Colloids (.001mm)....	33.0	26.0	48.0	21.0	25.0	22.0	23.0
<u>Proctor Compaction</u>							
Max. dry weight, lb/cuft	88.0	87.4	85	89.6	85.6	85.2	84.4
Optimum Moisture %	28.6	30.9	31.3	28.4	31.2	32.3	32.4
Voids ratio.....	.915	.895	.951	.855	.924	.961	1.01

and extent of such reaction and of the degree of stabilization achieved depends upon the physical and chemical character of this surface as well as on the properties of the stabilizing agent. The susceptibility of soils to the different methods of stabilization is, therefore, influenced not only by physical factors such as gradation, but also, and sometimes dominantly, by surface-chemical factors; of the latter the clay mineral composition, the exchangeable ions, and the type and amounts of organic matter are of special importance. Space limitations prevent detailed treatment of the complex physico-chemical interactions between stabilizers and the surfaces of solid soil constituents; however, reference is made to the tables accompanying the paper on "Soil-Stabilization" (These Proceedings) and to publications cited in that paper.

Physico-chemical phenomena are important not only in the case of admixtures foreign to the soil, but also in granular stabilization. Well known is the setting up of a graded mixture of siliceous aggregate and lateritic clay, and of limestone aggregate and podsollic clay. Such cementation occurs whenever positively and negatively charged soil materials are mixed. This phenomenon is illustrated by the data in Table 5 which are concerned with dry strength and slaking resistance of Putnam and Cecil soils and their mixtures.

Some of the most important problems in soil engineering are related to the physical chemistry of soil organic matter and to microbial processes. The problem of living and dead organic matter in soil is quite complex because of the large number of different types of organic molecules and systems involved as well as because of structural interrelationships among these organic molecules and between the organic matter and the clay minerals. However, for most engineering purposes it is sufficient to know the total amount of organic matter and its relative distribution among the seven chemical groups shown in Table 6 for the Loess Pampeano top- and sub-soils (8). In these particular soils, the content in cellulose and hemicellulose is low and that in proteins and lignins high, showing an advanced state of decomposition of plant organic matter due to great bacterial activity, favored by the presence of mineral plant nutrients. Organic matter of the type and in the amount contained in the Loess Pampeano top soil is very favorable for any waterproofing stabilization, as long as further bacterial action is prevented (9,10).

Soils in which organic matter is accumulated under conditions of low bacterial activity, stymied by lack of mineral activators, contain a relatively large proportion of celluloses and hemicelluloses. This type of organic matter is almost always objectionable.

TABLE 5

Data on Tensile Strength and Slaking
Resistance of Putnam and Cecil Soils
and their combinations

P Putnam Soil

C Cecil Soil

Composition	Tensile Strength in lb/sq in.	Slaking time (2) in minutes
Putnam Soil	90	9
P ₉ C ₁	167	8
P ₈ C ₂	157	9
P ₇ C ₃	147	20
P ₆ C ₄	142	29
P ₅ C ₅	140	17
P ₄ C ₆	113	15
P ₃ C ₇	107	19
P ₂ C ₈	97	14
P ₁ C ₉	82	11
Cecil Soil	47	13

- 1) Data represent averages of three determinations;
- 2) Method of Russian pedologists.

Inorganic stabilizers containing lime, may, if added to such soils, in amounts insufficient to kill the microbial organisms, result in their activation by the Ca-ion and, through a connected chain of events, may weaken rather than improve a subgrade soil. The general detrimental effect of organic matter on portland-cement products is too well known to require special emphasis. It should be emphasized, however, that knowledge of soil organic matter and of microbial phenomena not only assists in understanding the unpleasant consequences of their presence, but that this knowledge points out a way to a practical utilization of the organic matter, already contained in a soil, for coordinated action with other stabilizers. This is one of the principles on

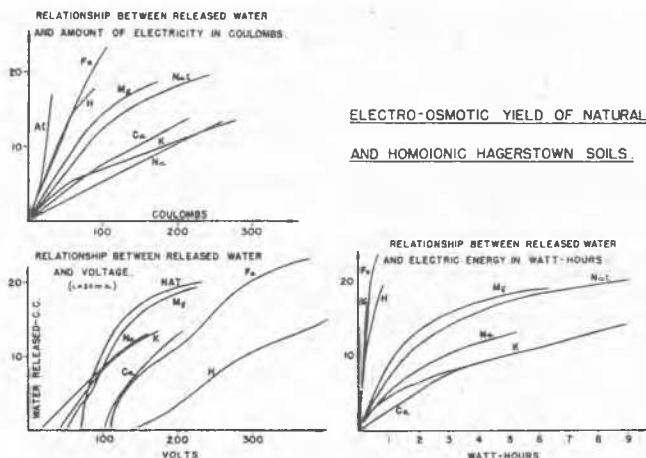
which the so-called natural method of soil-stabilization is based 11).

Within recent years, electro-osmosis has met with increasing use and interest on the part of the soil engineer. Theoretically pure electro-osmosis is an interfacial phenomenon and, consequently, depends on the physico-chemical characteristics of the interface. Electro-osmosis in normal soils is rendered impure by ionic conductance and transference; the latter, of course, also represent or depend on physico-chemical properties, such as base exchange capacity, type of exchangeable ions, degree of ionic dissociation and others 12). The effect of different exchange ions on electro-osmotic phenomena is shown in Graph 2.-

TABLE 6

Nature of the organic matter in loess pampeano soils% of total
organic matter

Constituent	Topsoil	Sub-soil	Top-soil	Sub-soil	Difference
Total organic matter.....	4.5	1.95			
Protein.....	47.00	42.75	1.615	0.833	0.782
Lignin.....	37.40	42.05	1.588	0.625	0.963
Celluloses.....	4.8	9.6	1.96	1.87	0.09
Hemicelluloses.....	5.8	10.4	0.261	0.202	0.059
Sugars, amino-acids, etc...	2.88	1.52	0.129	0.029	0.100
Wax, resins, alkaloids, etc.	0.89	2.11	0.040	0.041	
Wax, resin-like fatty substances.....	1.20	1.57	0.054	0.030	0.024



Electro-osmotic yield of natural and homoionic hagerstown soils.

GRAPH 2

CONCLUSIONS

The facts and data presented in this paper and in the references cited should make clear the importance of physico-chemical phenomena in governing actual soil properties and in aiding or obstructing soil stabilizing measures. While there cannot exist intelligent soil stabilization without physico-chemical understanding, it does appear that the body of soil mechanics itself needs to absorb more and more physico-chemical principles and knowledge if it is to keep healthy; otherwise, it might degenerate into increasingly mathematical mental fictions, or return to its former status of a primitive art, unrelated to available scientific knowledge.

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