Chemical Interactions on the Compressibility of Remoulded Kaolin

Les Interactions Chimiques sur la Compressibilitė du Kaolin Remaniė

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SYNOPSIS - Wiyh the object of investigating the effects of physico-chemical variables on the properties of pure clays, it has been analyzed the compressibility of remoulded Kaolin in the presence of interstitial liquids of different chemical composition. It has been shown that the presence of different exchangeable ions in the soil solution leads to variable values of the compression index, whereas the consolidation coefficient is practically constant. The change of the compression index has been set in connection with the physico-chemical properties of the interstitial fluids, that is the electrolyte concentration, the ' pH ', the size of hydrated ion, the ion valence, the conductivity, the static dielectric constant and the viscosity. In the light of the obtained results the interaction forces have been investigated on the ground of physical properties of soil solids, pore fluids and ions. The analysis of long-range chemical interactions (Diffuse double-layer repulsion, Van der Waals attraction and ionic forces) and short-range forces (mainly repulsion from adsorbed fluid layers) has shown the relative importance of both the mechanical and the chemical interaction forces with the regard to the compressibility of pure clays.

INTRODUCTION

It has been pointed out in recent years that the compressibility of fine-grained soils depends not only on the mechanical properties of its constituents, but also on the chemical composition of the interstitial liquid. The physico-chemical analysis of the forces of interaction among the phase constituents of clay soils has been carried out both on the base of the existence of double-layer and Van der Waals forces (Bolt, 1956; Van Olphen, 1963) and in account of the solid to liquid and solid to solid interactions (Rosenqvist, 1955; 1959; Martin, 1960; Lambe, 1960; Schofield and Sampson, 1954; Christensen and Wu, 1964) . The combined electromechanical interaction forces in clay soils have been developed on a mathematical base by Moore and Mitchell (1974): both electrostatic and electrodynamic forces of interaction have turned out a function of the static dielectric constant of the pore-fluid.

The purpose of this Paper is to show the results of a set of oedometer tests on remoulded Kaolin with different pore-fluids characteristics and to analyse the experimental data on the ground of the physico-chemical properties of the used interstitial fluids.

General Characteristics of studied Clay

Experimental tests were performed using a material that was on sale already fractionated and depurated.
The X-ray spectrographic analysis showed a content of kaolinite of about 85% and a percentage of illite of about 15%, the weight of amorphous matter beeing negligible. The kaolinite showed various degrees of crystallization: from regular-partly irregular to irregular-partly regular.

The index properties of this material, that we will name from now on simply "kaolin", are presented in Table n° I : grain-size analysis and specific gravity tests have been repeated many times to make sure of the kaolin homogeneity, that is of the fact that the experimental ranges of the properties result only from the variations in the pore-fluids characteristics.

Pore-water Solutions and pore-fluids

In order to have the expected variety of interstitial fluids characteristics, both solutions of different salts and fluids were used. The properties of the used solutions are specifyed in Table n° II:

Sample n°	Properties of kaolin	Consistency			C_c	C_s	C_s/C_c
		w_L	w_P	w_S			
A	% <20 μ: 100% % < 2 μ: 67 % % < 1 μ: 55 % d_h = 0.8 μ γ_s = 2.59 (g/cmc) S_s = 3.3 m^2	65	36	29	0.644	0.206	0.320
B		73	44	28	0.871	0.198	0.227
C		70	42	27	0.799	0.187	0.234
D		69	39	29	0.714	0.168	0.235
E		60	38	30	0.541	0.175	0.323
F		61	39	30	0.570	0.193	0.338
G		58	38	29	0.575	0.225	0.391
H		64	44	28	0.614	0.118	0.170
I		63	38	28	0.604	0.168	0.278
L		58	37	29	0.557	0.179	0.321
M		72	42	35	0.786	0.187	0.238
N		==	==	==	0.639	0.197	0.308
O		122	63	==	0.599	0.162	0.270
P		==	==	==	0.718	0.230	0.320
Q		==	==	==	1.112	0.021	0.019

TABLE N° I - Summary of consistency limits and oedometer compression tests.

Sample	Cation	Electrolyte concentration	pH	Conductivity ($\mu\sigma$/cm x 10^5)	Number of tests
A	==	==	7.3	7 x 10^{-5}	6
B	Na	0.1	11.3	1.18	4
C	Na	1.0	10.7	1.10	4
D	Na	2.5	9.5	1.00	4
E	Na	0.1	5.7	0.53	4
F	Na	1.0	5.2	0.59	4
G	Na	1.7	5.0	0.63	4
H	Fe	1.0	0.7	0.58	3
I	Al	1.0	3.2	0.74	3
L	Na	1.0	5.4	9 x 10^{-2}	3
M	NH_4	1.0	5.6	0.70	2

TABLE N° II - Pore-water characteristics.

Sample	Pore-fluid	Chemical Formula	Static dielectric Constant	Number of tests
N	Acetone	CH_3COCH_3	21	2
O	Glycerol	$C_3H_8O_3$	42	4
A	Water	H_2O	80	6
P	Formamide	$HCONH_2$	110	2
Q	Air	==	1	4

TABLE N° III - Pore-fluid characteristics.

the variations of the pH and conductivity values were obtained by selecting suitably the salt and his concentration. The cations of the solutions were chosen in order to have also a certain range in the valence and size of the hydrated ions. The pore-fluids used are presented in Table N° III : they have a wide range of static dielectric constant and this was the aim of the choice.

In the whole were used 11 pore-water solutions with 4 different cations and 5 pore-fluids: the number of tests performed on each of these is detailed in Tables N° II and III .

Experimental Procedure

The specimens were prepared by mechanically remoulding the oven-dried Kaolin with each of the pore solutions or fluids, in such a way as to have a particles structure that was from the beginning as similar as possible for all the prepared specimens, the fabric affecting significantly the compressibility behaviour of clay soils.

The weights of used fluid and oven-dried Kaolin has been such as to have in all specimens an initial ratio of 110 - 120 % , that is of about twice the liquid limit value.

The obtained slurries of Kaolin were then poured into the oedometer cells and consolidated at pressures slowly increasing up to 0.1 Kg/cm^2 during a period of three days. The fluid used to fill the oedometer cell was the same pore-fluid of the specimen, but with a ion concentration of twice lower to avoid, as much as possible, a difference between the osmotic pressures of the free pore-water in the sample and of the solution in the cell.

EXPERIMENTAL DATA AND INTERPRETATION .

Consistency

The detail of the experimental results in the determination of the consistency limits are related in Table N° I , where are quoted the mean values of the index properties come out from many tests.

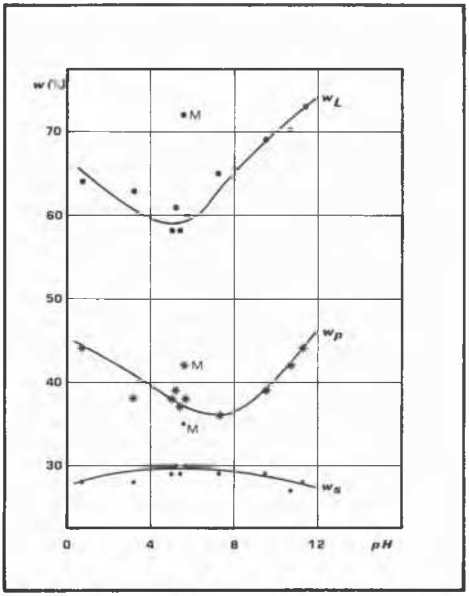

Fig. 1 - Relationship between consistency limits (w_L , w_P , w_S) and solution's pH .

The effect of both cation valency and hydrated ion size resulted negligible with respect to the influence of pH value. The diagram of Fig. 1 shows the relationship between consistency limits, expressed as a water percentage, and the pH value of the used solution.

Liquid and plastic limits show a minimum respectively in connection with a pH value of about 5.5 and 7, that is for solutions lightly acid or neutral. The shrinkage limit seems to have a maximum for a pH value of about 6, but his variation is very little if compared with those of the other limits. The trend of the relation curves is quite regular, with the exception of the values pertinent to the Kaolin remoulded with NH_4Cl (Sample M). The effect of ionic concentration, as molarity, is clear in the basic range, while in the acid field the results are rather dispersed. The higher values of liquid and plastic limits obtained for the Kaolin remoulded with glycerol have to be set in relation with the viscosity of the fluid rather than with other properties.

The trend of these experimental data may be explained only with a decrease of the attraction or an increase of the repulsion forces between the particles as the pH values become, from a quasi-neutral value, more and more high both in the acid and basic range, but with a more plain behaviour in the basic field.

Compressibility

The specimens, consolidated at a pressure of 0.1 Kg/cm^2, were then tested in the usual manner to determine the compressibility and consolidation characteristics. The experimental results, expressed as compression (C_c) and swelling (C_s) indexes, are presented in Table N° I, in therms of weighted mean of the obtained data.

The values of the consolidation coefficient 'c_v' have not been listed because they show a very little and irregular variation with the pore-fluids properties: from 1.0 to 1.5 x 10^{-3} cm^2/sec. Only the coefficient of consolidation obtained for the Kaolin remoulded with glycerol has been ten times lower (1.2 x 10^{-2} cm^2/sec), and this even if the viscosity is higher in the glycerol than in the water: the glycerol yet do not form a double-layer around the particles and this do make easier the expulsion of the fluid out of the sample during the consolidation process.

The relationship between compression index and solutions conductivity are showed in Fig. 2 : the increase of the conductivity leads to a relative increase of the compression index, at least as from a value of about 0.5 x 10^5 $\mu\sigma$; in the range of lower conductivity values the relation is only hypotetical, because the lack of experimental data.

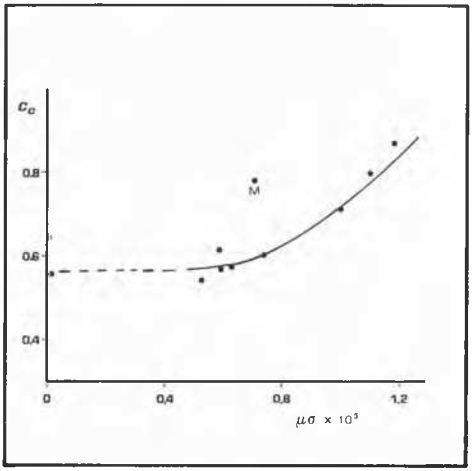

Fig. 2 - Relationship between compression index (C_c) and conductivity ( ).

More interesting is the relation between C_c and pH values: the trend of the curve throughout the experimental points is similar to that of liquid limits in the w - pH diagram, but is more cleare.

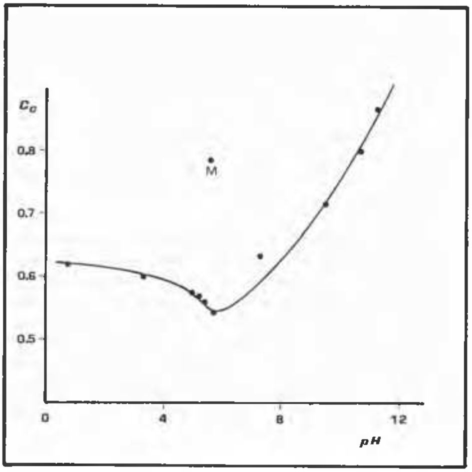

Fig. 3 - Relationship between compression index C_c and solutions pH .

The curve (Fig. 3) shows a C_c minimum at a pH value of about 6: from this point the relation is hardly linear in the range of basic values with high increases of the compression index; in the acid range the C_c increase is smaller, with an asymptotic trend to a C_c value of about 0.62 . The effect of ions concentration 'c' is completely opposite in the two branches of the curve: an increase in the basic range of the ionic concentration coincide with a decrease of the compression index (Samples B, C and D), while in the acid range we obtain an increase, even if little, of the C_c value (Samples E, F and G) .

The general trend of this curve shows that, from a central point (pH = 6), an increase in the pH value leads to higher values of the attraction forces and this is magnifyed by the decrease of the ionic concentration: the higher the electric potential between particles at the same distance the lower the concentration. The distance at wich the resultant of the attraction and repulsion potential energy has the maximum value will then decrease with both the ion concentration and pH increases, the last beginning from a value of about 6 .

The decrease of pH values, always from about 6, coincide also with an increase of the attraction forces, but it is lower and coupled with the increase of the ionic concentrations: the former effect is due probably to the combined action of the ion valency that, increasing from 1 to 3, develops a lower electric potential with the distance from the particle surface, and of the general strong decrease of the cation size; both these facts correspond to a decrease of the attraction forces. The last effect may be due to the fact that kaolinite can develop positive charge in acid solutions by dissociation of the surface hydroxyl ions and then decrease the net force between the particles.

The effect of the static dielectric constant of the medium between the particles is shown by the diagram of Fig. 4 . The general trend is nearly parabolical: the compression index shows a minimum in connection with a ε value of about 40, increasing then for both lower and higher static dielectric constant.

This behaviour agrees the experimental results of Moore and Mitchell (1974): beginning from a value of 4 (the static dielectric constant of clay particles), the net force between Van der Waals attraction forces, due to the perturbation of the electromagnetic fields, and electrostatic repulsion forces increases regulary with the static dielectric constant until an ε value of about 35; above this value the net force decreases because of the concomitant decrease of Van der Waals forces and constant increase of electrostatic forces. (Fig. 5) .

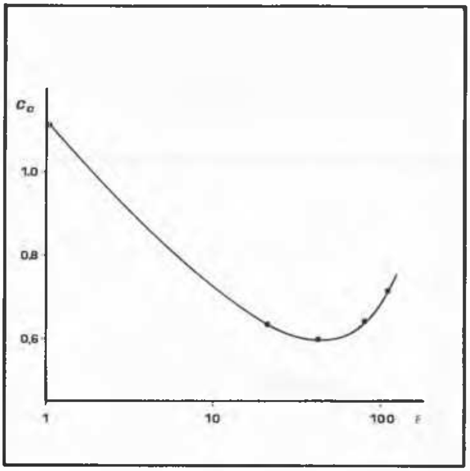

Fig. 4 - Relationship between compression index C_c and static dielectric constant

The relating behaviour of tested Kaolin samples will be then as explained in Fig. 4, that is coinciding with the trend of the net forces values between the particles.

The swelling index C_s shows (Fig. 6) decreasing values with the lowering of the pH beginning from

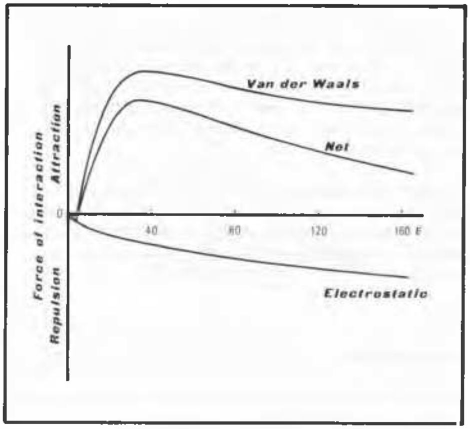

Fig. 5 - Interaction forces between soil particles (Moore and Mitchell, 1974).

the pH value of about 5.5 - 6.0 : the attraction forces will develop then more and more rapidly than the relating repulsion forces. The swelling index is practically constant above this value of pH: the effect of the increase in the attraction forces in this range of pH is probably annihilated by the high distance between the particles in the tested specimens (more than 800 Angstrom).

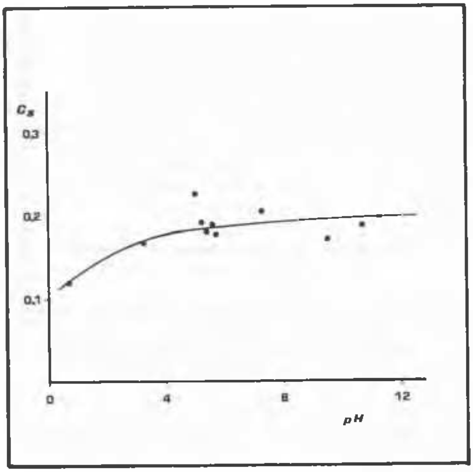

Fig. 6 - Swelling index C_s and solutions pH interrelationship.

The relationship between swelling index C_s and static dielectric constant is shown in Fig. 7. The trend of the graph, also in this case, reflects the value of the net force between the particles: the minimum C_s value coincides always with a dielectric constant of about 40; lower or higher values of ε lead to higher swelling indexes because of the concomitant decrease of the net interparticle forces.

A set of the consolidation curves, obtained during the development of this research, is presented in Figures from 8 to 13, collected in groups showing the influence of single pore-fluids properties.

CONCLUSIONS

A set of oedometer tests have been carried out on samples of remoulded Kaolin using different pore-fluids with the aim of recognize the compressibility behaviour of clay soils in relation to the physical and chemical properties of the interstitial fluids.

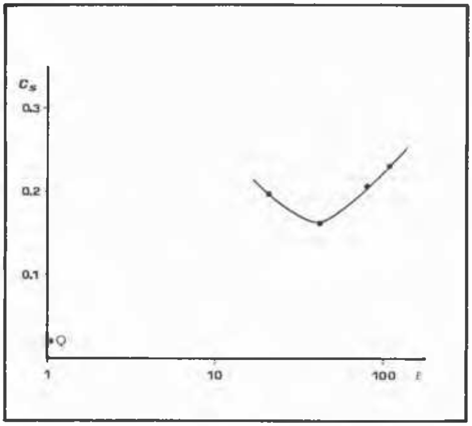

Fig. 7 - Influence of static dielectric constant on the swelling behaviour of remoulded Kaolin.

The most important variations of the compression index C_c are related both to the pH and the static dielectric constant values of the pore-fluids. The compression index shows aoways a minimum, higher values resulting from the increase or the decrease of both the pH and static dielectric constant, with respect the former to a value of about 5.5 - 6.O, the last to a value of about 40 .

The effect of static dielectric constant is very evident by computing the electrostatic and electrodynamic forces with the well-known formulae given by Bolt (1956), Van Olphen (1963) and Dzyaloshinskiĭ (1961) and Moore-Mitchell (1974) .

More complex results the relationship between compression index and pH values of the solution in the pore spaces. The development of attraction and repulsion forces is complicated by the combined effects both of cation valency and size.

Furthermore we have a different development of dissociation of surface active materials with a variation of the acidity, that is a different value of the charge density on the particles surface. The total negative charge is then somewhat increased by the degree of acidity, but the kaolinite can, on the contrary, develop a positive charge in acid solutions because of the dissociation of the surface hydroxyl ions.

The balance of the attraction and repulsion forces is therefore complex and the calculations are very complicated.

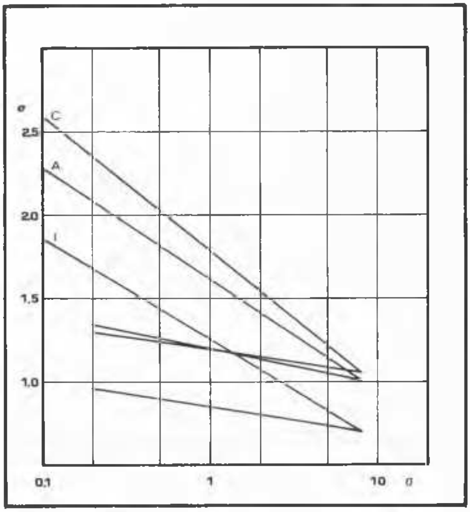

Fig. 8 - Consolidation curves of remoulded Kaolin: different solutions pH .

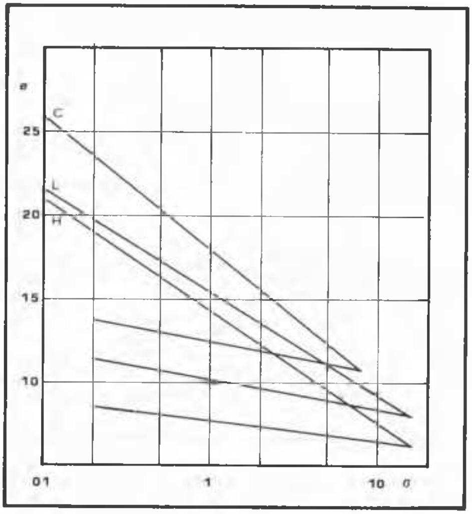

Fig. 10 - Consolidation curves of remoulded Kaolin: different solutions pH .

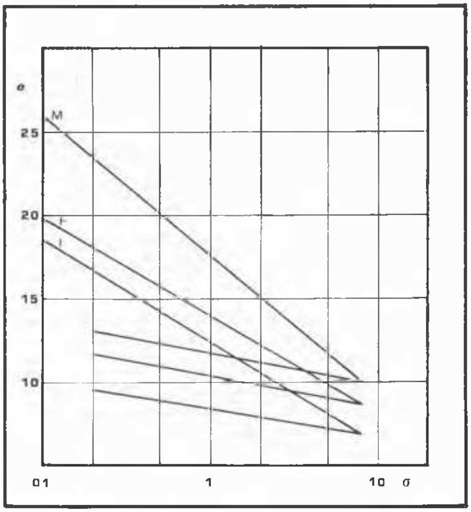

Fig. 9 - Consolidation curves of remoulded Kaolin: different solutions pH .

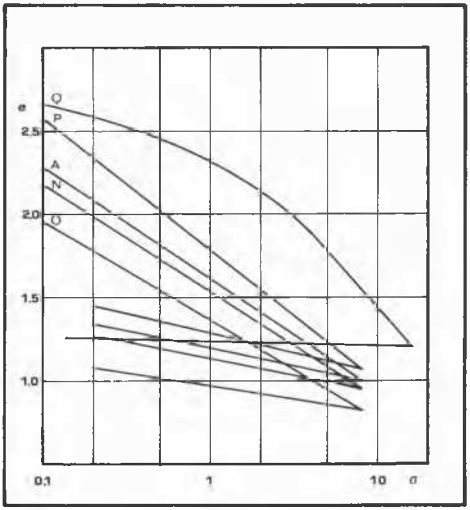

Fig. 11 - Consolidation curves of remoulded Kaolin: different static dielectric constant of pore-fluids.

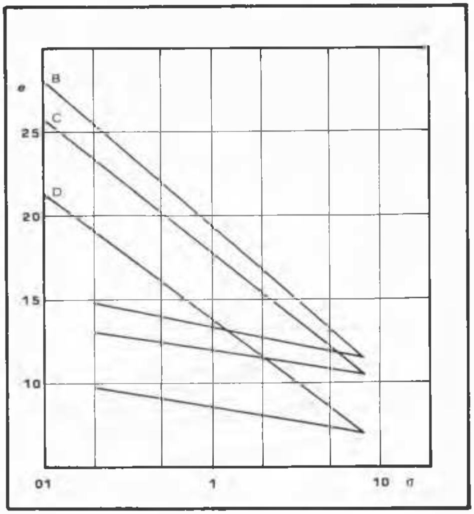

Fig. 12 - Effect of ionic concentration on consolidation curves of remoulded Kaolin : basic solutions.

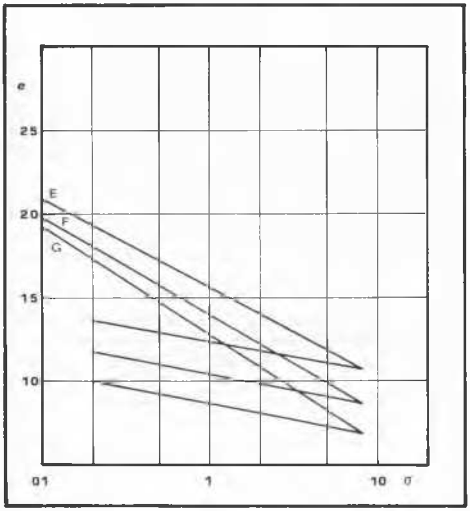

Fig. 13 - Effect of concentration on consolidation curves of remoulded Kaolin: acid solutions.

APPENDIX I

List of symbols

c : ionic concentration, as molarity
C_c : compression index
C_s : swelling index
d_h : harmonic mean ( )
e : void ratio
S_s : specific surface (m^2)
w : water content (%)
w_L : liquid limit (%)
w_P : plastic limit (%)
w_S : shrinkage limit (%)
γ_s : specific gravity of solids (g/cm^3)
ε : static dielectric constant
σ : pressure (Kg/cm^2)

APPENDIX II

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