Influence of electrolytes on stress strain behaviour of kaolin

Influence des électrolytes sur le comportement contrainte-déformation du kaolin

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SYNOPSIS: Kaolin which is a ceramic material has been studied by other researchers as regards its stress strain behaviour when mixed with water, and also the kinertic parameters had been studied. Influence of chemical additive on stress strain behaviour of Kaolin is not known. This paper reports the influence of water, and the electrolytes pyrosulphuric acid $H_4P_2O_7$, pentasodium triphosphate $Na_5P_3O_{10}$ and Arquard 2HT 75% on Kaolin. Mixture of Kaolin with water, was used as control. Results show that the yield surfaces of Kaolin with electrolytes are not on Roscoe state boundary surface, but from envelopes above and below it.

1 INTRODUCTION

Clay, is the oldest ceramic material and consists mainly of fine mineral particles of large surface areas with or without admixed organic matter. Most of the work on clay has been concentrated on Kaolin. (Roscoe and Burland 1968). In order to generalise the studies for clays, it is necessary to use a number of clays, and some additional studies have been made on Gault clay by Thompson (1962), Osho (1970) and on weald clay by Hambly (1969). The studies can be further generalised by changing the particle surface interactions in a clay. This paper is concerned with the amount of variation in the stress strain behaviour of Kaolin which can be caused by changing the electrolyte in the pore fluid.

Temperature effects of dehydroxylation enthalpy and also cementious properties of amorphous compounds in clays, will not be considered in this paper.

2 PREVIOUS WORK AND CHOICE OF CLAY

Lambe (1954) from his work on compacted fine grained soils found that sodium tetraphosphate $(Na_6P_4O_{13})$, reduced compressibility, permeability and frost susceptibility, and increased the optimum compacted density. The higher optimum density did not however lead to higher strength than for the soil without dispersants compacted to its optimum density.

Bolt (1956) made a comparison between the one dimensional consolidation curves of highly orientated montmorilionite and illite clays with sodium chloride (NaCl) and calcium chloride $(CaCl_2)$ electrolytes, and showed that the compressibility of the clays could be accounted for quantitatively by the consideration of the interaction between the electric double layers formed on the clay particles.

Olson (1963) carried out consolidated - undrained 'triaxial' tests on sedimented samples of sodium illite with variable concentration of sodium chloride (NaCl), and concluded that the stress path tangency point was more satisfactory for failure criterion than either the maximum deviator stress or the maximum ratio of the principal stresses. However his studies on shear and consolidated characteristics on sedimented calcium and sodium illite, showed that the e - p relationships were affected by the pore electrolyte concentration of calcium chloride $(CaCl_2)$, but the rebound curves were independent of the pore electrolyte concentration.

The work in this paper differs from the previous work in that it attempts to generalise the effects of electrolytes on the stress strain behaviour of clays, using Spestone Kaolin.

3 PROPERTIES OF SPESTON KAOLIN

Spestone Kaolin was chosen because most of the Cambridge research studies have been made on it and therefore many data have been compiled which will be useful for comparison. Spestone Kaolin contains about 90% of mineral Kaolinite and about 10% of the mineral muscovite, and this makes it free of impurities. The cation exchange capacity is 3.85 milli equivalents per 100g of Speston Kaolin, and this indicates a rather inactive clay. Spestone Kaolin has liquid limit w_L 74%, plastic limit w_P 42%, activity 0.44 and specific gravity 2.61.

4 SELECTION OF ELECTROLYTE

Russel (1950) postulated that the adsorption of cations in clay must be regarded as taking place in such a way that a series of oriented water dipoles lie between the cations and the colloidal particle. They form the double layer. Metallic cations can be arranged in a Hofmeister series according to their capacity for being adsorbed on negative particles. Each ion in this series can displace the one to its right in competition for adsorption centres.

$$H^+ > Al^{+++} > Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} > NH_4^+ > Na^+ > Li^+$$

The thickness of the double layer diminishes to the left and increases to the right. The cation exchange has its parallel in the case of anions.

$SO_4^{--} F^- < NO_3^- < Cl^- < Br^- < I^- < CN^- < PO_4^{---}\ P_2O_7^{----}$

$< P_3O_{10}^{-----} < CO_3^{--} < OH^-$

Their adsorption is weaker than cations, since it is confined to the positively charged edges of clay particles. Loading the clay particles with ions on the right of the list (especially OH^-) increases the negative charge. Those to the left especially SO_4^{--} diminish the negative charge and increase flocculation.

It is not the aim of this paper to make a close study of the chemistry of the electrolytes or the nature of chemical or physical interaction in the clay-water-electrolyte systems. Nevertheless some consideration was given to the chemistry of the electrolytes in order to select electrolytes which would have a measurable influence on the stress strain properties of the clays. Using the above series as a guide, Pyrophosophoric acid $H_4P_2O_7$, Pentasodium triphosphate, $Na_5P_310_{10}$ and Arquard 2HT 75% were used from a selection of eighteen electrolytes, with marked effects on the liquid limit using five percent electrolyte by weight of the air dried Kaolin. Kaolin with five percent pyrophosophoric gave the least liquid limit of 32.8% with plasticity index of 3.2%. The liquid limits for Kaolin with five percent Pentasodium triphosphate and five percent Arquard 2HT 75% were 47.7% and 94% respectively. The plasticity indices were 16.7% and 40% respectively.

5 SAMPLE PREPARATION AND TEST PROCEDURES

Solutions of the electrolytes were prepared by mixing predetermined amounts of electrolytes with sufficient distilled water to bring the clay to a moisture content of 160%. The amounts of powdered electrolyte added to the water (i.e. 1¼%, 5% and 10%) were determined as a percentage by weight of air dried Kaolin. After adding the electrolyte to the distilled water, the solution was agitated for fifteen minutes in a Parvalux electric mixer at 6000 r.p.m. to ensure a homogeneous solution. The electrolyte solution was then mixed with Kaolin in a pug mill under a vacuum of 50.8cm of mercury.

5.1 Consolidation and swelling behaviour under isotropic stress

After 1.D consolidation under about 157.5kN/m², an isotropic pressure of 210kN/m² was applied. Silicone oil was the cell fluid. The sample was then isotropically consolidated by a 70kN/m² isotropic stress increment every 12 hours to an isotropic stress of 630kN/m². The reverse procedure was followed in the swell back, in that the decrease of stress was 70kN/m² every 12 hours. The final swelling pressure was 35kN/m². The sample diameter was 38.1mm and length was 76.2mm. The test results are as shown in Figure 1.

5.2 Undrained stress controlled axisymmetric shear tests

Axial loads were applied in increment of 2.27kg, every twelve hours until failure occurred. The pore pressure was measured by Bell and Howell 0 - 1050kN/m², flush mounted type transducer. The axial strains were measured by a dial gauge reading 0.0254mm per division. The test results are as shown in Figures 2, 3 and 4.

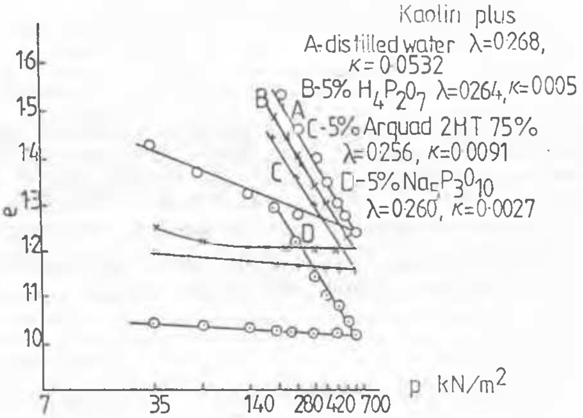

Figure 1. Isotropic consolidation and swelling tests on Kaolin with distilled water and 5% by weight of each electrolyte.

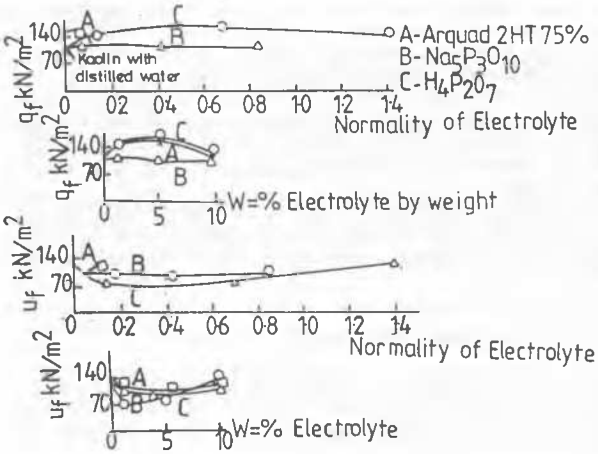

Figure 2. Shear stress, pore pressure at failure and concentration of electrolytes in undrained stress controlled 'triaxial' tests on Kaolin.

5.3 Drained stress controlled axixymmetric shear tests

Drained axisymmetric shear tests were conducted on normally consolidated Kaolin-water and Kaolin-electrolyte samples. The samples were tested between free ends and drainage was from the bottom of the sample through 6.35mm diameter aerox VI porous stone which was previously boiled and deaired. Drained tests were conducted after initial isotropic consolidation stresses of 210kN/m² and 420kN/m² respectively. The liquid in the burette for measuring volume change, was covered

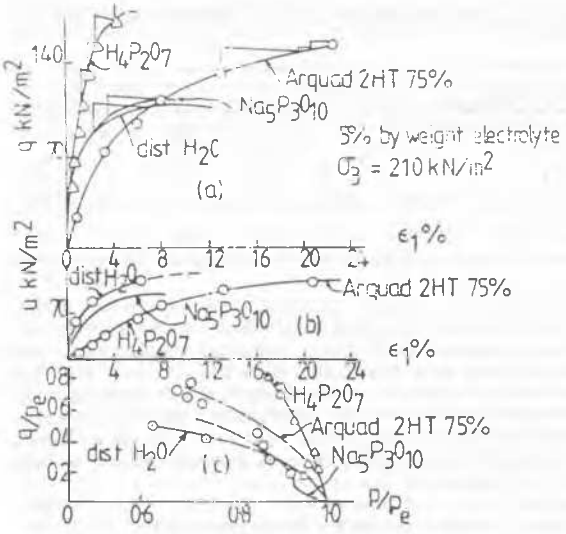

Figure 3. q,u vs ε_1 and q/p_e vs p/p_e in undrained stress controlled 'triaxial' test on Kaolin with 5% of each electrolyte

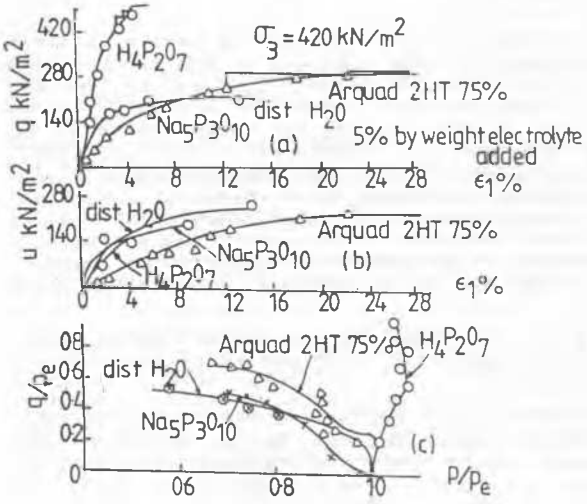

Figure 4. q,u vs ε_1 and q/p_e vs p/p_e in undrained stress controlled 'triaxial' tests on Kaolin with 5% of each electrolyte.

with a paraffin dye to prevent evaporation. The loading was the same as for undrained tests. Test results are as shown in Figures 5 and 6.

6 SELECTION OF PARAMETERS

The soil parameters that are required for the state boundary are those given by Roscoe and Burland (1968). The frictional parameter M, for compression tests is as follows:

$$M = \frac{6 \sin \phi'}{3-\sin \phi'} \qquad (1)$$

For ultimate strength condition q_f is given by

$$q_f = M.P_f \qquad (2)$$

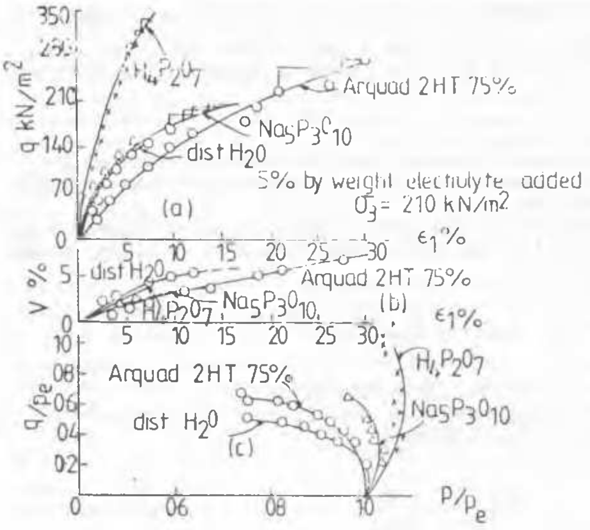

Figure 5. q,v vs ε_1 and q/p_e vs p/p_e in drained stress controlled 'triaxial' tests on Kaolin with 5% of each electrolyte.

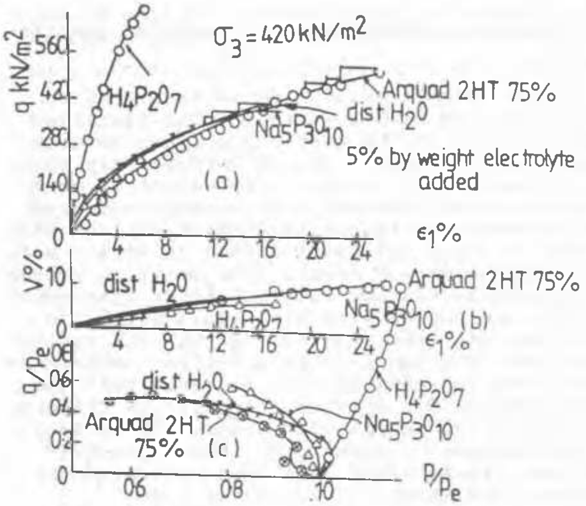

Figure 6. q,v vs ε_1 and q/p_e vs p/p_e in drained stress controlled 'triaxial' tests on Kaolin with 5% of each electrolyte.

The stress parameters used in the Cambridge axi-symmetric triaxial theory (in which $\sigma_2' = \sigma_3'$) are the deviatoric compression

$$q = \sigma_1' - \sigma_3' \qquad (3)$$

and the mean normal stress

$$p = \frac{1}{3} (\sigma_1' + \sigma_2' + \sigma_3') \qquad (4)$$

The isotropic consolidation equation is as follows:

$$e = e_o - \lambda \log_e p \qquad (5)$$

where e is the void ratio, p is the isotropic consolidation pressure, e_o is the void ratio when $p = 1$ and λ is a soil constant. The form of equation for the rebound lines is as follows:

$$e = e_o - \kappa \log_e p \qquad (6)$$

the λ and κ values are fundamental parameters in the formation of the Cambridge stress strain theories.

Roscoe and Burland (1968) two-dimensional representation of the state boundary surface is shown as

$$p/p_e = \left(\frac{M}{M^2 + \eta^2}\right)^{(1-\kappa/\lambda)} \qquad (7)$$

where η is stress ratio q/p.

The pore pressure coefficient A_f (Skempton, 1954) is as follows:

$$A_f = \frac{u_f}{q_{max}} \qquad (8)$$

where u_f is the pore pressure corresponding to q_{max}.

7 DATA ANALYSIS AND DISCUSSION

7.1 Isotropic consolidation - swelling behaviour

The virgin consolidation line is displaced to the left of the line for Kaolin with distilled water as shown in Figure 1. The lines however remain parallel with λ values varying only between 0.25 and 0.27. Using 5% by weight of each electrolyte the greatest displacement occurred with Pentasodium triphosphate which was the electrolyte to have the least effect on stress strain relations during shear. The swelling curves are noticeably flatter with all three electrolytes than for Kaolin with distilled water, i.e. the values are less than for Kaolin with electrolytes than for Kaolin with distilled water. At critical state, equation (7) suggests that the state boundary for electrolytes will be different from that of Kaolin with water. The relationships between λ, plasticity index, plastic limit and liquid limit have been postulated by Schofield and Wroth (1968) of the form

$$\begin{aligned} \lambda &= A.w_I/100 \\ &= B.\left(\frac{w_p}{100} - 0.09\right) \\ &= C.\left(\frac{w_L}{100} - 0.09\right) \qquad (9) \end{aligned}$$

where the values of A,B,C given by Schofield and Wroth for Kaolin are respectively 0.585, 0.92 and 0.36. Values of A,B,C are given for Kaolin with 5% of each electrolyte are shown in Table 1. There is therefore considerable variation in these factors A,B,C with different electrolytes.

7.2 Influence of electrolyte concentration

Stress controlled undrained shear tests on Kaolin samples consolidated to 210kN/m² were carried out at concentrations of 0, 1¼%, 5% and 10% of each electrolyte. It was found as shown in Figure 2, that an optimum shear strength was reached with 5% by weight of the electrolytes Pyrophosphoric acod amd Arquard 2HT 75%. The corresponding normality of the electrolytes are about 0.7 and 0.05 respectively. For the Pentasodium triphosphate, the largest value of the maximum shear strength was reached at a concentration of 1¼% by weight, at corresponding normality of pentasodium triphosphate of about 0.09.

Table 1. The values of A,B,C parameters for Kaolin.

Electrolyte	w_L	w_p	λ	A	B	C
H_20	74.0	42	0.28	0.88	0.86	0.43
$Na_5P_30_{10}$	47.7	31.0	0.23	1.38	1.04	0.59
$H_4P_20_7$	32.8	29.6	0.21	6.6	1.02	0.88
Arquard 2HT	94.0	53.5	0.26	0.64	0.57	0.31

A rather similar behaviour to that described above was found by Moum, Sopp and Loken (1968), who tested effect of different chloride salts on the undrained shear strength of chloritic - illitic quick clays.

7.3 Influence of electrolytes on frictional properties

The frictional properties of the Kaolin in shear were altered by the addition of the electrolytes. This is as shown in Table 2. It can be seen that 5% Pyrophosophoric acid with Kaolin increases M by 50% in both drained and undrained tests, above the value for Kaolin with distilled water only. Arquard 2HT 75% in a concentration of 5% with Kaolin increases the M values by 11% in undrained tests and 24% in drained tests over the distilled water value. Pentasodium in 5% concentration decreased the undrained M value by 11% and has no influence in the drained value.

Table 2. Frictional properties of Kaolin with distilled water and 5% by weight of each electrolyte.

Electrolyte	H_20	$Na_5P_30_{10}$	$H_4P_2O_7$	Arquard 2HT 75%
ϕ'	20.8	18.8	29.3	23.0
ϕ_d	18.6	18.6	27.5	22.8
M_u	0.81	0.72	1.17	0.90
M_d	0.72	0.72	1.09	0.89

7.4 Influence of electrolytes on pore pressures in undrained stress controlled tests

All three electrolytes at the three concentrations used, had the effect of reducing the pore pressures during shear deformation compared to samples of Kaolin with distilled water only. Pore pressure parameters are as shown in Table 3. The initial consolidation was 210kN/m². Reduction in pore pressure of this magnitude, i.e. more than 50% reduction with pyrophosophoric acid, is of considerable importance for example, in compaction of clay fills. The increases in values of q_{max} and ϕ', ϕ_d and M would also be significant in this connection.

Table 3. Pore pressure parameters of Kaolin with distilled water and 5% by weight of each electrolyte.

Electrolyte	H_2O	$Na_5P_3O_{10}$	$H_4P_2O_7$	Arquard 2HT 75%
u_f/σ_o	0.62	0.50	0.42	0.48
A_f	1.2	1.0	0.5	0.7

7.5 Volume changes in drained stress controlled tests

In general the volume changes during shear distortion under drained conditions were less for Kaolin with electrolytes than for Kaolin with distilled water. This is consistent with the pore pressure behaviour discussed above as both pore pressure and volume change during shear reflect the dilantancy properties of the soil. The test results are as shown in Table 4.

Table 4. Volumetric strain of Kaolin with distilled water and 5% by weight of each electrolyte.

Electrolyte	H_2O	$Na_5P_3O_{10}$	$H_4P_2O_7$	Arquard 2HT 75%
$v_{max}\%$	6.2	3.8	4.1	6.3(at ε_1=25%)

7.6 q-p-e relationship in stress controlled 'triaxial' tests

The state boundary represented on q/p_e vs p/p_e plot for Kaolin with distilled water has been the subject of study by a number of Cambridge workers (e.g. Roscoe and Thurairajah (1966), Roscoe and Burland (1968)).

Roscoe and Thurairajah (1966) postulated that a unique yield surface exists for undrained, partially drained and fully drained tests. This unique surface in (σ', τ, e) space was confirmed for Kaolin for drained and undrained tests in the simple shear apparatus (SSA). However undrained and drained axisymmetric triaxial compression tests on Kaolin gave two independent state boundary surfaces and critical state lines for undrained and drained 'triaxial' tests. Roscoe and Thurairajah then explained that since uniform dilation throughout the sample can be accomplished in the SSA, and not in the triaxial samples, then if the void ratio can be correctly measured in the most deforming part of the samples in triaxial drained and partially drained tests, one unique surface and one critical state line would exist in (q,p,e) space for all compression tests regardless of the dialation allowed to the samples of a given clay.

In the undrained plots in Figure 3c and Figure 4c, it can be seen that the initial consolidation pressure had virtually no influence on the general shape of the curves.

In drained tests, however, the curves at the two different pressures of 210kN/m^2 and 420kN/m^2 show some fairly marked differences (see Figure 5c and Figure 6c). The general shape (but not the size) of the curves for 5% pentasodium triphosophate are similar to that for distilled water, but in the undrained tests (see Figure 4c) the pentasodium triphosphate curves show a reverse curvature. The Arquard 2HT 75% curves are similar in shape to distilled water in both drained and undrained tests except for a small reverse curvature in the drained test at 420kN/m^2, which is probably not significant.

The most marked departure from the behaviour of Kaolin with distilled water is shown by Pyrophosphoric acid, which in undrained tests, distorts, with only a small change in p throughout shear. This behaviour is quite consistent at both 210kN/m^2 and 420kN/m^2. In the drained test at 210kN/m^2, the same electrolyte gives only a small change in p/p_e during shear and is thus behaving in a manner corresponding to the undrained behaviour. In the drained test at 420kN/m^2 the value of p/p_e (with Pyrophosophoric acid) increases slightly during the test but in general the behaviour corresponds to that discussed above.

It is of interest to note that this shear distortion with only small changes in p/p_e in the case of the Kaolin with Pyrophosophoric acid is accompanied by a 75% increase in q_{max} over the value for Kaolin with distilled water, which corresponds to an increase of ϕ' from 20.8 to 29.3, and a 50% increase in M from 0.81 to 1.17. In Figures 7 to 10, the end points of all stress controlled 'triaxial' tests are plotted as e vs $\log_e$ p. The virgin consolidation line (VCL) is also shown. For drained tests on Arquard 2HT 75%, where no q_{max} is reached, the values of e and p at an axial strain of 25% have been taken.

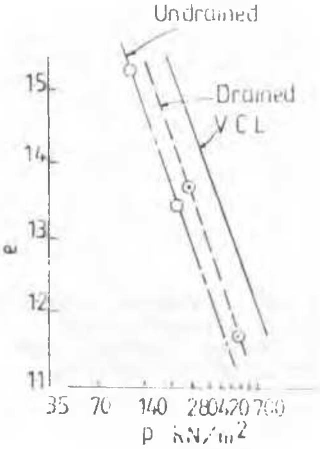

Figure 7. Void ratio and mean principal effective stress for Kaolin with distilled water showing virgin consolidation line and lines through end points for undrained and drained 'triaxial' tests.

Referring to Figure 7, straight lines drawn through the two plotted points corresponding to q_{max} for each test condition gives lines which are approximately parallel to V.C.L. The lines for the drained and undrained tests are displaced relative to each other, indicative, that a unique e vs $\log_e$p condition is not reached in these two types of test. The slope λ of the lines for undrained and drained tests are resp-

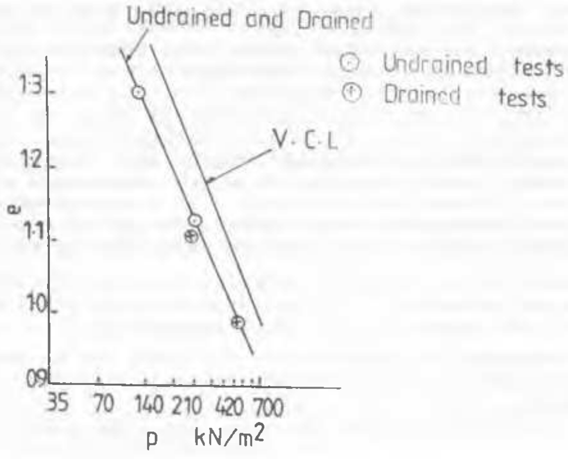

Figure 8. Void ratio and mean principal effective stress for Kaolin with 5% pentasodium triphosphate showing virging consolidation line and line through end points for undrained and drained 'triaxial' tests.

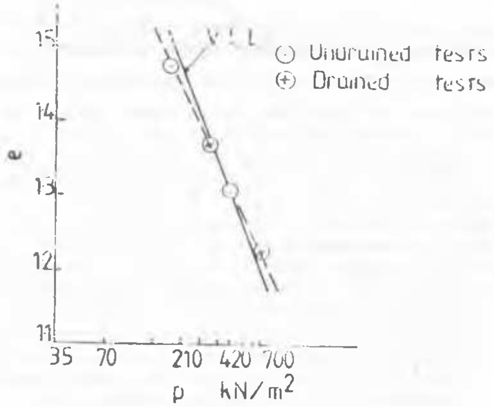

Figure 9. Void ratio and mean principal effective stress for Kaolin with 5% pyrophosphoric acid showing virgin consolidation line and line through end points for undrained and drained 'triaxial' tests.

ectively 0.28 and 0.28 compared with a value of 0.27 for V.C.L.

In Figure 8, the end points of tests on Kaolin with 5% Pentasodium triphosphate are shown and the two undrained points and one drained point lie on a single straight line which is nearly parallel to the V.C.L. The other drained point is slightly displaced from this line. The straight line drawn through the three points gives λ = 0.23 compared with 0.26 for V.C.L.

All the four end points for 5% Arquard 2HT 75% in undrained and drained tests as shown in Figure 10, fall on or close to a straight line with slope λ = 0.26 compared to 0.25 for V.C.L.

Hvorslev (1937) showed that the peak shear stress, τ_f, occuring at failure of saturated remoulded clay is a function of the effective

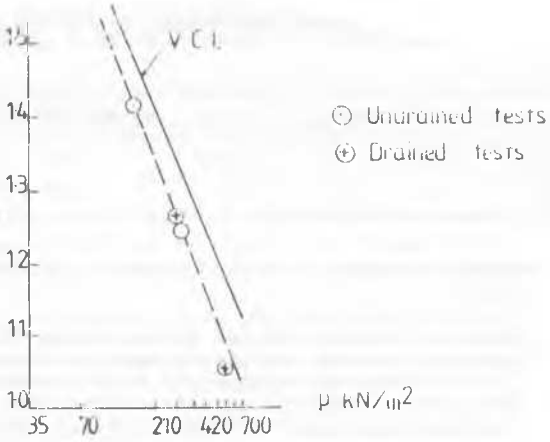

Figure 10. Void ratio and mean principal effective stress for Kaolin with 5% Arquard 2HT 75% showing virgin consolidation line and line through end points for undrained and drained 'triaxial' tests.

normal stress σ_f' on, and of the void ratio e_f in the plane of failure at the moment of failure, and is independent of stress history of the clay. The Hvorslev criterion of failure is expressed for a given soil by the equation

$$\tau_f = \mu_o \sigma_f + \nu \exp(-B e_f) \qquad (10)$$

where μ_o, ν and B are constants for the particular soil. Unfortunately Hvorslev's relationship can only be used to predict the strength at failure, if the failure values of the normal stress and void ratio are known, and these are difficult to assess especially in triaxial tests.

8 CONCLUSION

It has been shown in this paper that small amounts of electrolytes added to Kaolin have a marked influence on the shear-strain-dilation properties. This is the case even with a relatively inactive clay such as the Spestone Kaolin.

In view of the marked influence of electrolytes on Kaolin behaviour, it is important that in any programme of laboratory testing to determine the stress properties of clays, the soil chemistry must be very carefully controlled.

The value of λ is a constant of the soil and is independent of the type of electrolyte in the pore fluid. However the value of κ is dependent on the electrolyte in the pore fluid.

The effect of pyrophosophoric acid is to reduce markedly the pore pressure and the volumetric strain, and increase q_{max} and ϕ', ϕ_d and M. This behaviour will be of considerable importance in the compaction of clay fills.

The effect of organic electrolyte Arquard 2HT 75% on Kaolin in 'triaxial' tests was to increase markedly the axial strain at which q_{max} occured and at the same time to increase the values of q_{max} and ϕ', ϕ_d and M. In some cases a peak q value was not reached even up to 30% axial strain. In view of this behaviour, it is possible that the additon of this type of electrolyte to clay fills might make them more able to resist cracking due to differential movements within the clay fill and on the boundary of the clay fill.

NOTATION

p'	Mean normal effective stress
p	Mean normal stress
p_e	Mean normal stress on isotropic virgin consolidation
q	Shear stress
λ	gradient of normal consolidation line in e-lnp' space
κ	gradient of swelling in e-lnp' space
w_L	Liquid limit
w_P	Plastic limit
M	Stress ratio q/p' at critical state
η	Stress ratio q/p' at any state below critical state
ϕ'	Effective angle of soil internal friction
ϕ_d	Drained angle of internal friction
u	pore pressure
v	volumetric strain
ε_1	Axial strain

REFERENCES

Hambly, E.C. (1969). "Plane strain behaviour of soft clay". Ph.D. thesis, University of Cambridge, United Kingdom.

Hvorslev, M.J. (1922). "Uber die Festigkeitseigneschaften gesterter bindiger Boden". Ingenorviden skabelige, Skrifter, 4 No. 45, Copenhagen. (English Translation No. 69-5. U.S. Waterways Expt. Stn. Vicksburg, Miss 1969).

Lambe, T.W. (1954). "Improvements of soil properties with dispersants". Reprinted from the Journal of the Boston Society of Civil Engineers.

Roscoe, K.H. & Burland, J.B. (1968). "On the generalised stress strain behaviour of 'wet' clay". Engineering Plasticity, (Ed. J. Heyman & F.A. Leckie), Cambridge University Press, 535-609.

Roscoe, K.H. & Thurairajah, A. (1966). "On the uniqueness of yield surfaces for wet clays". Proc. Int. Symp. Rheology and Soil Mech. of the Int. Union of Theor. and App. Mech., Springer-Verlag, Berline, 364-381.

Russel, D.A. (1950). Trans. Brit. Ceramic Soc., 49, 297.

Schofield, A.N. & Wroth, C.P. (1968). Critical State Soil Mechanics. McGraw-Hill Book Company, London, United Kingdom.

Moum, J., Sopp, O.I. & Loken, T. (1968). "Stabilization of undisturbed quick clay by Salt Wells". Norwegian Geotech Inst. Pub., 81.

Olson, R.E. (1963). "Shear Strength Properties of a sodium illite". Journal of the Soil Mechanics and Foundation Division, Proc. of Am. Soc. of Civil Engineers, 89, 183-208.

Osho, P.A. (1970). "The Influence of Electrolytes on the Stress Strain Behaviour of Soils". M.Sc. Thesis, Cambridge University, Cambridge, United Kingdom.

Skempton, A.W. (1954). "The pore-pressure coefficients A and B". Geotechnique IV, 143-147.

Thompson, W.J. (1962). "Some deformation characteristics of Cambridge Gault Clay". Ph.D. Thesis, University of Cambridge, United Kingdom.