

EFFECTS OF EXCHANGEABLE CATIONS ON HYDRAULIC CONDUCTIVITY OF A MARINE CLAY

S. NARASIMHA RAO AND PAUL K. MATHEW

Ocean Engineering Centre, Indian Institute of Technology, Madras-600 036, India

Abstract—A laboratory study of the hydraulic conductivity (HC) of a marine clay with monovalent, divalent and trivalent cations revealed large differences in HC. The exchangeable cations employed in this study are Na, K, NH₄, Mg, Ca and Al in order of increasing valency. An interpretation of the results derived from consolidation tests suggests that HC is significantly affected by the valency and size of the adsorbed cations. An increase in the valency of the adsorbed cations leads to quicker rates of consolidation and higher HC, while, for a constant valency an increase in the hydrated radius of the adsorbed cations results in a lower rate of consolidation and HC. The reduction in HC was related to the dispersion and deflocculation of clay. Lower valency and higher hydrated radii of the exchangeable cations enable the double layer repulsive forces to predominate, thereby increase dispersion and deflocculation.

Key Words—Consolidation, Dispersion, Exchangeable cation, Hydraulic conductivity.

INTRODUCTION

Hydraulic conductivity (HC) is a measure of the ease with which a fluid passes through a material. It is one of the fundamental engineering properties of a soil and the knowledge of which is required in seepage, settlement and stability calculations. The HC for a given soil depends on size and shape of the particles, void ratio, arrangement of the pores and soil particles, properties of the pore fluid and the amount of undissolved gas in the pore water (Michaels and Lin 1954, Lambe 1954). In fine grained soils, HC under saturated conditions is controlled by the microstructure of the soil matrix which in turn depends on the type of the clay mineral present in the soil, the composition of the exchangeable cations and the electrolyte concentration in the pore water system. The ease with which flocculation, deflocculation and swelling of a clay mineral take place affects the structure of the pores and, hence, the HC (Quirk and Schofield 1955).

There is a necessity felt by environmental geotechnical engineers to alter the HC characteristics of the soils using different chemicals offering various cationic systems and in view of this the study of cation adsorption and ion exchange has evinced a lot of interest in the field of HC of marine clays. In this experimental study an attempt has been made to evaluate the importance of exchangeable cations in regulating the HC of a marine clay. Adsorption of cations having different hydrated radius and valency by the fine grained soils are the two important factors to be considered in proposing any mechanisms dealing with differences in HC of fine grained soils. Wada and Beppu (1989) recommended treatment with Al to smectitic clay for its efficiency in increasing the HC and help in the decrease of exchangeable Ca, Mg and K. Shainberg *et al* (1987)

observed that the effect of exchangeable potassium percentage (EPP) on the HC of smectites depended on the charge density of clays. The HC of smectites having low charge density changed markedly when leached with dilute solutions as the EPP of clay increased. It has also been observed that HC decreases with increasing exchangeable sodium percentage (ESP) and decreasing salt concentration. From the reported results it can be seen that there is no definite influence of potassium on HC and this may be due to possible variation in the soil mineralogy and sample preparation techniques. As per Ahmed *et al* (1969) and Quirk and Schofield (1955) HC is related to exchangeable cations in the following order $Ca = Mg > K > Na$. However, some researchers report larger aggregates of greater stability in potassium saturated soils than in soils saturated with divalent cations (Cecconi *et al* 1963, Ravina 1973), suggesting that potassium in the exchange sites increases soil HC. Quirk and Schofield (1955) also suggested that the swelling of clay particles could result in total or partial blockage of the conducting pores. It is known that swelling in clayey soils increases with a rise in the percentage of monovalent exchangeable cations. Deflocculation, dispersion and clay movement into the conducting pores are also responsible for the plugging of the soil pores (Quirk and Schofield 1955). The importance of dispersion in soil HC has been recognized by several investigators (Frenkel *et al* 1978, Pupisky and Shainberg 1979, Shainberg *et al* 1981).

The objective of the present study is to investigate the effect of exchangeable cations on the HC of a marine clay. This work reports the results of one dimensional consolidation tests on a marine clay homoionized with a series of monovalent, divalent and trivalent cations. The mechanisms controlling the HC of clays are presented and discussed.

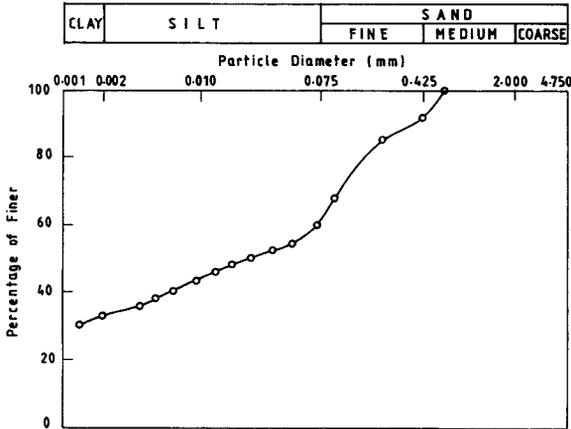


Figure 1. Grain size distribution curve for untreated marine clay.

MATERIALS AND METHODS

The marine clay used to study the effect of exchangeable cations on HC was collected from a site on the east coast of India. The soil deposited in this area is a soft marine clay. The Indian marine clays are Pleistocene to Recent in age; deposited in salty or brackish environments (Mohan and Bhandari 1977). Grain size distribution curve obtained from hydrometer analysis (as per ASTM D 422-63, 1989) of the marine clay studied is shown in Figure 1. X-ray powder diffraction (XRD) patterns of the clay fraction were obtained using a Philips diffractometer and $\text{CoK}\alpha$ radiation. The dispersed clay fraction separated by sedimentation under gravity was centrifuged on a glass slide in a high speed centrifuge and the XRD patterns were recorded as shown in Figure 2a. Figure 2b shows the XRD pattern obtained for ethylene glycol saturated sample which confirms the expandable phase. The mineralogical analysis of the clay carried out by comparing the obtained XRD patterns with Brown's Index card (1961) and the standard ASTM (1991) powder diffraction file indicates the presence of clay minerals swelling chlorite, kaolinite and illite. Feldspar and quartz constitutes the silt and sand fraction.

The exchangeable cations in the marine clay were determined by displacing the ions with 1 N NH_4OAc buffered at pH 7.0 (Jackson 1967). The NH_4OAc leachate was analyzed directly by flame emission using inductively coupled argon plasma. Determination of NH_4 was done by colorimetric method using Nessler's reagent (Vogel 1978). The results of the analysis are presented in Table 1.

Homoionic forms of marine clay with Na, K, NH_4 , Mg, Ca and Al adsorbed cations were prepared by treating a 100-g portion of the clays with 1.0 liter of a 1.0 M solution of the appropriate metal chloride. The suspensions were stirred over night. After settling for a

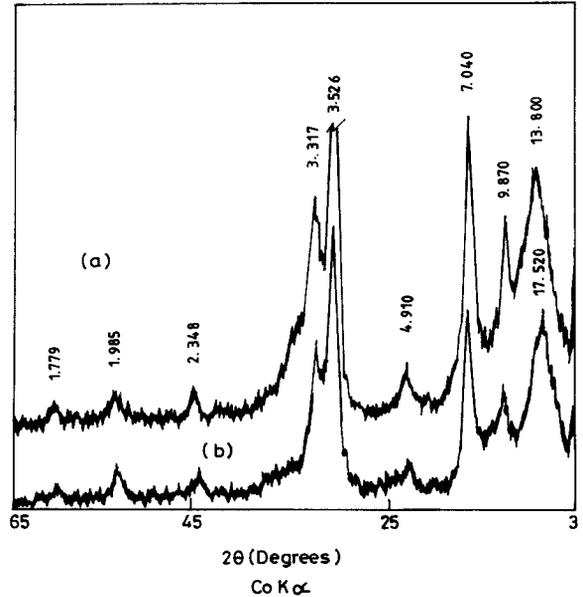


Figure 2. XRD pattern of clay fraction in marine clay. (a) Untreated (b) ethylene glycol saturated.

period of two to three hours, the supernatant liquor was decanted and the clay was filtered with a Whatman filter circle of diameter 120 mm. The clay was then washed several times with 50-ml aliquots of 60 vol. % IMS (industrial methylated spirits) until the filtrate gave no detectable chloride precipitates on addition of AgNO_3 solution. The entire procedure was repeated six times before each homoionic clay sample was dried at 60°C and stored in stoppered bottles.

The HC was determined from consolidation test using a standard oedometer test system. This type of testing was adopted by many investigators (Newland and Allely 1960, Mesri and Olson 1971, Budhu *et al* 1991). Since soft clays are very sensitive to stress system, oedometer test system can be conveniently used to find the HC at different stress levels. In the present study all specimens for consolidation tests were prepared at a very soft consistency (at liquid limit) using distilled water as pore fluid. In the oedometer test system 20 mm thick and 60 mm diameter samples were sandwiched between two porous stones. The specimens were allowed to equilibrate with distilled water for 24 hours prior to the initiation of the tests. The rate of compression due to the expulsion of pore water was measured using a standard mechanical type of dial-gauges under different consolidation pressures. The fluid that is expelled from the sample during compression is allowed to drain from the cell in a vertical direction. All the tests were conducted at constant temperature in a closed room. The HC is calculated from the expression

Table 1. Exchangeable cations in untreated marine clay studied.

Cation	Cation concentration in meq/100-g
Sodium (Na)	9.381
Lithium (Li)	0.060
Potassium (K)	1.945
Ammonium (NH ₄)	0.260
Magnesium (Mg)	16.917
Calcium (Ca)	6.287
Barium (Ba)	0.017
Aluminium (Al)	0.021

$$k_p = \frac{c_v a_v \gamma_p}{1 + e} \quad (1)$$

where k_p is the hydraulic conductivity (cm/sec), c_v is the coefficient of consolidation (cm²/sec), a_v is the coefficient of compressibility (cm²/kg), γ_p is the unit weight of the pore fluid (kg/cm³) and e is the void ratio. Consolidation tests were carried out as per ASTM D 2435-80 (1989).

RESULTS AND DISCUSSION

Ion exchange is a surface chemical phenomena which is influenced by a number of variables. The distribution of ions in the exchange solution and the exchanger is modified by the desired ions like Al, Ca etc. It is difficult to express ion exchange equilibria in a strict thermodynamic sense (Ferrell and Price 1978). Replacement of cation takes place when the cation concentration is increased in the pore fluid. This is to be expected, since cation exchange is a stoichiometric reaction and the laws of mass action would hold good (Grim 1953). In general, therefore, increased concentration of the replacing cation causes greater exchange by that ion. The exchangeable cations present in the untreated marine clay are given in Table 1. Mg is the predominant cation present and this is typical of a marine clay (Carroll and Starkey 1958). Table 2 shows the concentration of exchangeable cations in homoionic clays. In all the cases of homoionic clays the concentration of cations other than the desired system is less than 1 meq/100-g. Results show that all samples were nearly homoionic. It is also observed that the pH of the different homoionic

Table 2. Concentration of exchangeable cations in homoionic clays.

Clay type	Concentration of cations, meq/100-g					
	Na	K	NH ₄	Mg	Ca	Al
Na	33.254	0.146	0.185	0.312	0.314	0.021
K	0.233	22.203	0.167	0.235	0.267	0.013
NH ₄	0.209	0.200	19.752	0.114	0.118	0.019
Mg	0.229	0.395	0.145	20.211	0.180	0.015
Ca	0.042	0.182	0.167	0.016	24.086	0.007
Al	0.020	0.027	0.035	0.124	0.113	17.582

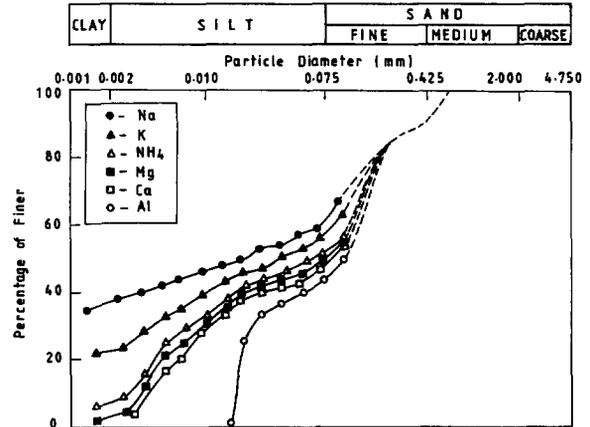


Figure 3. Grain size distribution curves for homoionic clays.

systems varies. The pH of Al clay is 4.34 and that of Na clay is 6.95. It has been reported by many (Schofield 1949; Grim 1953) that cation exchange capacity (CEC) is pH dependent and hence the cation sum varies in different homoionic systems.

Grain size distribution curves of homoionic clays obtained from hydrometer analysis are given in Figure 3 and from these curves large differences in the flocculation characteristics of homoionic clays can be seen. In clayey soils any changes in the adsorbed complex can induce significant changes in the double layer system and this can consequently affect the interparticle forces (van Olphen 1962). With the suppression in the repulsive force system, there is a tendency for the particles to flocculate and aggregate. With the increase in the valency of the adsorbed cations, the double layer thickness gets reduced. This can result in considerable changes in the average size of particles. The results presented in Figure 3 bring out considerable particle growth with increase in the valency. This particle growth may be as a result of aggregation of particles. For different adsorbed complex at the same valency, any reduction in the hydrated ion radius also suppresses the double layer and promotes particle growth. An approximate quantitative indication of the influences of factors affecting the thickness of the double layer is given by Mitchell (1993)

Table 3. Hydrated radius of cations (after Kielland 1937).

Cation	Hydrated ionic radius (Å)
Na	4-4.5
K	3.0
NH ₄	2.5
Mg	8.0
Ca	6.0
Al	9.0

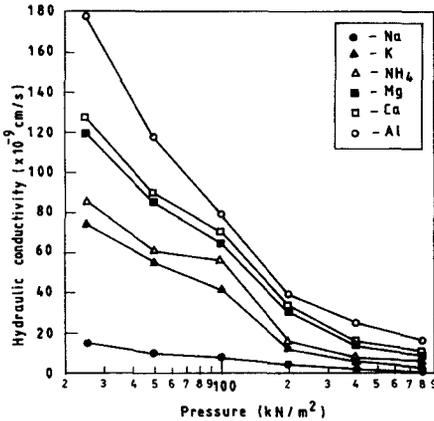


Figure 4. Variation of hydraulic conductivity with pressure.

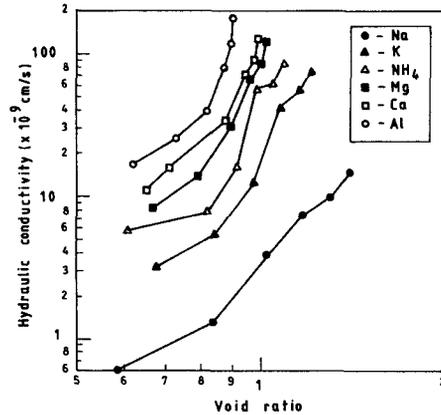


Figure 5. Variation of hydraulic conductivity with void ratio.

$$\frac{1}{K} = \left(\frac{DkT}{8\pi n_0 e^2 v^2} \right)^{1/2} \quad (2)$$

where $1/K$ is the thickness of double layer (\AA), D is the dielectric constant of the medium, k is the Boltzmann constant ($\text{erg}/^\circ\text{K}$), T is the temperature ($^\circ\text{K}$), n_0 is the electrolyte concentration (ions/cm^3), e is the unit electronic charge (coulomb) and v is the cation valency. From this relationship it may be noted that all other factors remaining the same, the thickness of the double layer decreases inversely with the valency. As the double layer thickness reduces attraction between clay particles increases leading to better flocculation. For a constant valency double layer thickness increases as the hydrated ion radius increases. The hydrated ion radii of the cations used in this study are given in Table 3 (Kielland 1937). Examination of the results presented in Figure 3 show that Al clay is in a flocculated state whereas Na clay is in a dispersed state. Flocculated state of all other clays is in between Al clay and Na clay.

The variation in HC with pressure is shown in Figure 4. The HC decreases with pressure for all the homoionic clays saturated with Na, K, NH_4 , Mg, Ca and Al. However at any pressure higher values are recorded for systems with higher valency. HC of Al clay is 12 to 13 times the HC of sodium clay at any pressure. Figure 5 shows the variation of HC with the void ratio. As expected HC increases with void ratio and these increases are small when sodium is the exchangeable cation. The reduction in HC with reduction in void ratio is as a result of: 1. reduced amount of void space for flow, 2. increased amount of diffuse double layers, 3. adsorption of fluid on the available void space and 4. probably as a result of induced re-orientation of the particles perpendicular to the direction of fluid flow (Quigley and Thompson 1966) thereby increasing the

tortuosity factor. The convergence of the curves at low void ratios indicates that the particles are being compressed into such close proximity that the void space is clogged by the presence of large concentration of hydrated cations.

It is known that the changes in the type of cations adsorbed and their valency and the changes in the electrolyte concentration can bring considerable changes in the particulate arrangement and the double layer thickness. It has already been brought out in Eq. (2) that the increases in the valency can cause considerable reduction in the thickness of double layer. It is also established that replacement of monovalent cations by higher order valency cations can change the particulate arrangement from dispersion to flocculation. The reduction in the double layer thickness and the tendency towards better flocculation can cause considerable increase in effective void size, that is to a change from micropores to macropores. So, because of this there can be considerable improvement in the HC. However at a constant valency the HC can decrease with increase in the hydrated ion radius. From the work of Ranganatham (1961) and Frenkel *et al* (1978) it can be seen that with changes in the particulate arrangement from dispersion to flocculation there is considerable improvement in HC. It is likely that thicker adsorbed layers on the surface of clay particles can impede the flow of water for two reasons, viz., 1. due to reduction in pore diameter and 2. due to physical interference of the movement of water against a surface of moderately oriented water such as would exist in the outermost molecular layers of the adsorbed water. Dispersion and swelling of clays within the soil matrix are interrelated phenomena, and this will change macropores to micropores which will reduce soil HC. Swelling reduces pore sizes and dispersion blocks pores. Plugging of the soil pores by dispersed clay particles is the major cause of reduced HC in case of cations with low valency.

CONCLUSIONS

Existing informations are limited to the effects of cation valency on HC in ideal systems like bentonite. This study demonstrates a marked influence of valency and hydration radius of the adsorbed cations on the hydraulic conductivity of a marine clay. Sodium saturated clay is approximately six times less permeable than potassium and ammonium clays. Saturation of marine clay with divalent cations increases its HC nine times in comparison with the sodium clays. The trivalent clay in turn is more permeable than the divalent clay.

REFERENCES

- ASTM. 1991. Index to the powder diffraction file. Published by Joint Committee on Powder Diffraction Standards, Philadelphia, Pennsylvania 19103.
- ASTM D 2435-80. 1989. Standard test method for one-dimensional consolidation properties of soils. Annual Book of ASTM Standards, Vol. 04-08, 283-287.
- ASTM D 422-63. 1989. Standard test method for particle size analysis of soils. Annual Book of ASTM Standards, Vol. 04-08, 83-92.
- Ahmed, S., L. D. Swindale, and S. A. El-Swaify. 1969. Effect of adsorbed cations on physical properties of tropical black earths. 1. Plastic limit, percentage stable aggregate and hydraulic conductivity. *J. Soil Sci.* **21**: 255-268.
- Budhu, M., R. F. Giese, Jr., G. Campbell, and L. Baumgrass. 1991. The permeability of soils with organic fluids. *Can. Geotech. J.* **28**: 140-147.
- Carroll, D., and H. C. Starkey. 1958. Effect of sea-water on clay minerals: Proceedings of the 7th National Conference on Clays and Clay Minerals, Washington, D.C., 80-101.
- Cecconi, A., A. Salazar, and M. Martelli. 1963. The effect of different cations on the structural stability of some soils. *Agrochimica* **7**: 185-204.
- Ferrell, R. E., Jr., and C. A. Price. 1978. An experimental study of cadmium ion exchangeability. *Clays & Clay Miner.* **26**: 41-44.
- Frenkel, H., J. O. Goertzen, and J. D. Rhoades. 1978. Effects of clay type and content, exchangeable sodium percentage, and electrolyte concentration on clay dispersion and soil hydraulic conductivity. *Soil Sci. Soc. Am. J.* **42**: 32-39.
- Grim, R. E. 1953. *Clay Mineralogy*. New York: McGraw-Hill Book Company.
- Jackson, M. L. 1967. *Soil Chemical Analysis*. New Delhi: Prentice-Hall of India, 82-89.
- Kielland, J. 1937. Journal of American Chemical Society **59**: 1675.
- Lambe, T. W. 1954. The permeability of fine grained soils. Special Technical Publication. American Society for Testing Materials **163**: 123-126.
- Mesri, G., and R. E. Olson. 1971. Mechanisms controlling the permeability of clays. *Clays & Clay Miner.* **19**: 151-158.
- Michaels, A. S., and C. S. Lin. 1954. Permeability of kaolinite. *Industry and Engineering Chemistry* **46**: 38-45.
- Mitchell, J. K. 1993. *Fundamentals of Soil Behavior*. New York: John Wiley and Sons, 118.
- Mohan, D., and R. K. Bhandari. 1977. Analysis of some Indian marine clays. International Symposium on Soft Clay, Bangkok, Vol. 1, 55-74.
- Newland, P. L., and B. H. Allely. 1960. A study of the consolidation characteristics of a clay. *Geotechnique* **10**: 62-74.
- Pupisky, H., and I. Shainberg. 1979. Salt effects on the hydraulic conductivity of a sandy soil. *Soil Sci. Soc. Am. J.* **43**: 429-433.
- Quigley, R. M., and C. D. Thompson. 1966. The fabric of anisotropically consolidated sensitive marine clay. *Can. Geotech. J.* **3**: 61-73.
- Quirk, J. P., and R. K. Schofield. 1955. The effect of electrolyte concentration on soil permeability. *J. Soil Sci.* **6**: 163-178.
- Ranganatham, B. V. 1961. Soil structure and consolidation characteristics of black cotton clay. *Geotechnique* **11**: 333-338.
- Ravina, I. 1973. The mechanical and physical behavior of Ca clay soil and K clay soil. *Berlin Ecol. Stud.* **4**: 131-140.
- Schofield, R. K. 1949. Effect of pH on electric charges carried by clay particles. *J. Soil Sci.* **1**: 1-8.
- Shainberg, I., R. Keren, N. Alperovitch, and D. Goldstein. 1987. Effects of exchangeable potassium on hydraulic conductivity of smectite-sand mixture. *Clays & Clay Miner.* **35**: 305-310.
- Shainberg, I., J. D. Rhoades, and R. J. Prather. 1981. Effect of low electrolyte concentration on clay dispersion and hydraulic conductivity of a sodic soil. *Soil Sci. Soc. Am. J.* **45**: 273-277.
- van Olphen, H. 1962. *An Introduction to Clay Colloid Chemistry*. New York: Interscience, 92-110.
- Vogel, 1978. *Vogel's Text Book of Quantitative Inorganic Analysis: 4th Edition*. Longman: English Language Book Society, 730-731.
- Wada, K., and Y. Beppu. 1989. Effect of aluminium treatment on permeability and cation status of smectitic clay. *Soil Sci. Soc. Am. J.* **53**: 402-406.

(Received 4 April 1994; accepted 7 November 1994; Ms. 2491)