

A STUDY ON THE DOMINATING MECHANISMS AND PARAMETERS INFLUENCING THE PHYSICAL PROPERTIES OF ARIAKE CLAY

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ABSTRACT: Extensive investigations have been carried out on the engineering behavior of Ariake clays. The range of variation of physical properties for Ariake clay is very high. A better understanding of the engineering behavior necessitates the understanding of their physical and physico-chemical behavior. The factors influencing the physical properties are the clay mineral type, percent clay size fraction, and the pore medium chemistry. Both ion concentration and type of ion can vary significantly. Comparison of Ariake clay with change in ion concentration has been examined with bentonite clay treated with artificial seawater and it has been found that two dominating mechanisms control their liquid limit behavior. As concentration and/or ion valence increase, flocculation takes place and attractive force increase, leading to increase in liquid limit. At the same time the diffuse double layer gets depressed decreasing the liquid limit. These two mechanisms oppose each other in influencing the liquid limit. However both mechanisms co-exist and depending upon the factors like relative proportion of various clay minerals present, percent clay size fraction and type and concentration of various ions, one of the mechanism dominates.

INTRODUCTION

Marine clay deposits of 15-30 m thick are widely distributed around Ariake bay, Kyushu, Japan. Large areas have been reclaimed for agricultural, industrial and other developmental activities. Extensive investigations have been carried out on the engineering behavior of Ariake clay (e.g. Miura et al. 1996; Hong and Tsuchida 1999). Figure 1 illustrates the Ariake bay with locations of which results are discussed in this article. A better understanding of the engineering behavior necessitates the understanding of their physical and physico-chemical behavior of fine-grained soils. Ariake clay, being a fine-grained soil, has been examined by many by studying their physico-chemical behavior and has made significant contributions (Egashira and Ohtsubo 1982; Ohtsubo et al. 1985; Ohtsubo et al. 1996; Rao et al. 1991 and 1993; Torrance and Ohtsubo 1995). Significant contributions have also been made to the understanding of the physical, physico-chemical and engineering behavior of other marine clays viz. Cochin marine clay (e.g. Jose et al. 1988a, and b), Mangalore marine clay (e.g. Rao 1974), marine clays of Canada (e.g. Torrance 1975) and Bangkok clay (e.g. Ohtsubo et al. 2000). In spite of significant contributions on Ariake clay as stated above, its physical and engineering behaviors are not very well understood. Further study on the physical, physico-chemical and engineering behavior of Ariake clay will become very useful if its behavior is compared with well-understood behavior of clay minerals and other similar clays subjected to different pore medium chemistry. Factors affecting overall behavior of marine clays are many

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and complex. One of the important physico-chemical parameters that affect the engineering behavior of clays of marine origin is the ion concentration. Ariake clay is subjected to a lot of leaching due to several reasons. Further understanding of the physical behavior gets better if the ion concentration effects are known. In this paper an attempt is made to bring out the significant parameters affecting the overall physical behavior of Ariake clay and to obtain insight into the mechanisms controlling the same. Attempt has also been made to make use of the results obtained on bentonite exposed to seawater in order to understand the mechanisms involved.

PHYSICAL PROPERTIES

Table 1a compares the physical properties of Norwegian, Canadian, Korean, and Hong Kong clays with Ariake clay. Table 1b presents the physical properties of Indian marine clays. The interesting aspect of comparison of different clays of Table 1a and 1b can be seen that the range of variation of properties of Ariake clay is significantly more. The range of liquid limit variation is 317%, plastic limit variation is 236%, Natural water content is 400%, plasticity index is 1200%, clay percent varies 684% and organic matter also varies significantly. This significantly large variation in their physical and in situ properties reinforces the need for better understanding the various parameters that may contribute to such large variations.

Figure 2 shows the plasticity chart representing Norwegian, Canadian, Ariake clay of Japan, and Indian clays. The Norwegian clays plot predominantly in the CL region, the Canadian clays in CH region, the Ariake clay in MH region and the Indian clay in the CH region. Most of the Ariake clays plot below the Casagrande A-line. Although in Fig. 2 it is seen that all marine clays plot around the A-line their physico-chemical and engineering behavior differ greatly. This aspect is discussed in the following paragraphs.

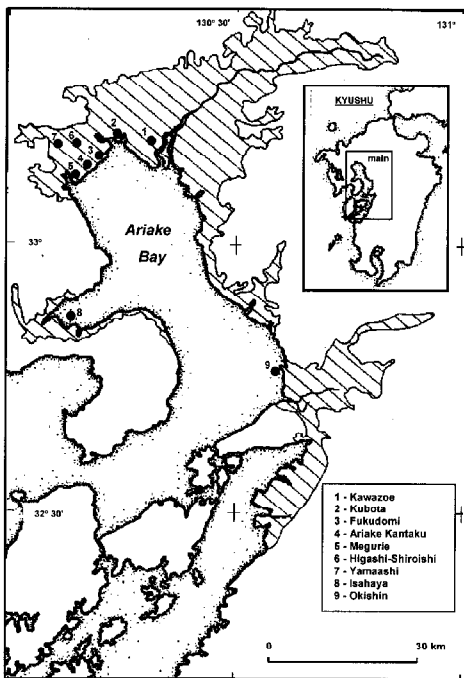


Fig. 1 Ariake bay with locations of soils used. The shaded area indicates the Ariake sediment

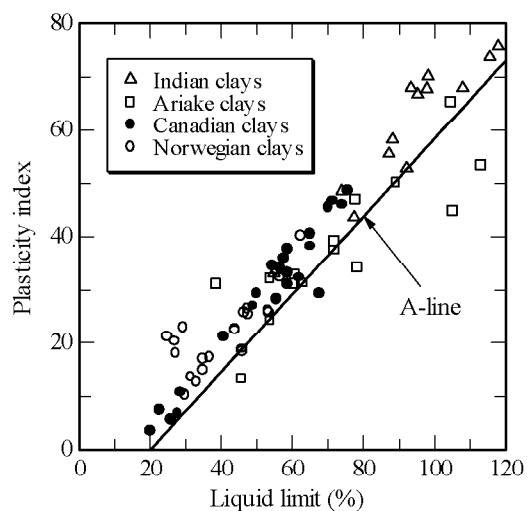


Fig. 2 Liquid limit vs. plasticity index for various marine clays areal extent of various marine clays

Table 1a Index and other properties of some marine clays

Properties	Location					
	Norwegian*	Ariake**	Japan	Canadian*	Korean*	Hong Kong*
Liquid limit (%)	21 - 57	53.5-169.5		32 - 60	31 -130	100 -140
Plastic limit (%)	16 - 30	25.0- 59.0		22 - 30	17 - 30	40 - 60
Natural water content (%)	32 - 44	50.9-200.0		40 - 90	27 -110	100 -120
Plasticity index	5 - 33	8 - 96		10 - 30	11 - 95	50 - 80
Clay (%)	35 - 65	11.4- 78.0		50 - 86	10 - 45	40 - 80
Sensitivity	3 -500	19 -500		10 ->1000	1 - 13	1.5- 80
Salt content (g/l)	0.2- 26	0.1- 34.7		1 - 35	2 - 10	25 - 80
pH	7 - 8	3.7- 9.0		9.3- 9.6	7.4- 8.0	4.5- 6
Organic matter (%)	1	1 - 18		5	3 - 7.0	4 - 30
Carbon (%)	< 1	< 4		10	5 - 11	2
CEC (meq/100g)	3 - 10	44 - 53		9 -13	-	-
Clay mineralogy	Illite	Smectite		Mica	Mainly	Illite
	Chlorite	Kaolinite		Illite	Illite	Kaolinite
	Quartz	Vermiculite		Chlorite		Smectite
	Feldspar	Mica, Chlorite		Vermiculit		Quartz
	Mica	Quartz		Feldspar		
	Amphibole	Feldspar		Quartz		
	Feldspar	Cristobalite		Amphibole		

*Sridharan (1999), ** Present study.

Table 1b Index and other properties of some Indian marine clays (Sridharan 1999)

Properties	Location				
	Visakhapatnam	Bombay	Madras	Cochin	Mangalore
Liquid limit (%)	65 -100	42 -100	80 - 86	83 -175	100 -176
Plastic limit (%)	40 - 45	26 - 60	24 - 28	33 - 60	62 - 72
Natural water content (%)	80 - 90	80 -125	73 - 75	76.4-128.8	105 -120
Plasticity index	25 - 50	25 - 40	52 - 64	49 -114	95 - 97
Clay (%)	40 - 70	38 - 80	25 - 77	36 - 48	36 - 38
Sensitivity	2 - 3	2 - 5	1 - 2	2 - 4	2 - 4
Salt content (g/l)	70 - 75	25 - 80	30	6 - 12	0.3- 1.5
pH	-	-	7 - 8.6	7.6- 8.23	~ 7.9
Organic matter (%)	-	1	0.2- 0.8	3 - 9.8	~12
Carbon (%)	-	47 - 55	1 - 5	3 - 23.5	3
CEC (meq/100g)	-	25	30 - 25	26 - 54	70
Clay mineralogy	-	Illite	Smectite	Smectite	Smectite
	-	Chlorite	Chlorite	Kaolinite	Kaolinite
	-		Illite	Feldspar	Feldspar
	-		Quartz	Mica, Calcite	Mica, Quartz
	-		Calcite	Hematite	Calcite, Hematite

MINERALOGY

It is widely reported that the clay mineralogy of Ariake clay is primarily smectite mineral followed by illite, kaolinite and vermiculite and chlorite (Egashira and Ohtsubo 1981 and 1982, and Ohtsubo et al. 1996). But it should be noted that the clay mineralogy has been studied for samples from clay size fraction. For example Egashira and Ohtsubo (1981) reported that the $<2 \mu\text{m}$ clay fraction of the Ariake marine mud contains the principal clay mineral as smectite followed by kaolinite, illite and vermiculite. It is to be noted that percent $<2 \mu\text{m}$ is 54%. Egashira and Ohtsubo (1982) mentioned that the clay fractions of Ariake by (Yamaashi, Higashi-Shiroishi and Ariake-Kantaku) contain considerable smectite, other clay minerals present are kaolinite, illite and vermiculite. The percent clay fraction is varied from 22% to 56%. In these clays the smectite content varied over a range of 33% to 42% in the clay size

fraction. Ohtsubo et al. (1982) further reported that the Ariake samples (Higashi-Shiroishi and Yamaashi) contained smectite as principal clay mineral accompanied by kaolinite, illite and vermiculite in the clay size fraction and the clay size fraction varied over a range of about 20 to 60%. Similar results have also been reported by Ohtsubo et al. (1985). It is seen from the above that the range of variation of percent smectite clay mineral in the over all soil fraction (not in the clay size fraction) is in the range of 10 to 23% which is quite low and need not be a dominating parameter. Other parameters like other clay minerals; non-clay size fraction and pore medium chemistry can also play an important role masking the role of smectite alone.

In all the above investigations while it was concluded that the principal clay mineral is smectite while their behavior with respect to their physical and engineering properties is that of non-swelling clay. In order to get insight into this, the authors have carried out careful X-ray diffraction tests as described below on three clay of Ariake bay, viz. Kawazoe, Kubota and Isahaya. X-ray diffraction pattern was obtained from field-moist samples. They were treated with 6% H_2O_2 to remove organic matter and were dispersed by 4% $NaPO_3$ to neutralize the charges on the smaller soil grains. The $<2 \mu m$ clay fraction was collected by repeated sedimentation and siphoning. Specimens for X ray powder diffraction (XRD) were prepared by taking duplicate clay suspension containing 50 mg clay. One was washed with 1 M $MgCl_2$ and the other with 1 M KCl . Excess salt was removed by washing with water. One cubic centimeter of water was added, and an aliquot of the suspension containing 30 mg of clay was dropped onto a glass slide (28×48 mm), air-dried, and X-rayed. The K-saturated specimen was heated at $300^\circ C$ and $550^\circ C$, and the Mg-saturated specimen was solvated with glycerol. Filtered $CuK\alpha$ radiation from a Rigaku diffractometer was used for XRD analysis (Whittig and Allardice 1986). Figures 3a and 3b show the XRD patterns (intensity versus diffraction angle θ) of the Mg-saturated-glycerol solvated (Mg-G), and K-saturated-air dried (K-Ad) of Kawazoe, Kubota and Isahaya. All of the clay fractions contain same clay minerals with different mineral concentration as reflected from intensity of XRD. The strong peak at 17.95-18.17 Å in the Mg-G specimen (Fig. 3a) and at 12.76-12.9 Å in the K-Ad specimen (Fig. 3b) reveals clearly that all of the clay fractions contain smectite (Sm). The presence of peak at 7.14-7.18 Å in the XRD patterns of Mg-G and K-Ad specimen (Figs. 3a and 3b), with the same intensity for all of the clay fractions indicate that presence of kaolinite (Kt) in all of the clay fractions with same quantity. Other clay minerals present are illite (It) and vermiculite (Vt) with different mineral concentration as reflected from intensity of XRD. Illite was detected from the peak at 10.02-10.06 Å in all of the XRD patterns. Vermiculite was detected from the peak at 14.29 Å in the Mg-G specimen (Fig. 3a) and at 15.3 Å in the K-Ad specimen (Fig. 3b). The silt and fine sand fractions contain quartz, feldspars, and cristobalite. Cristobalite and quartz were detected from the peak at 4.04 Å and 3.34 Å respectively in the K-Ad specimen (Fig. 3a) (Wada 1966). Moreover, there is gibbsite peak at 4.85 Å in the Mg-G specimen (Fig. 3a).

Wada (1966) stated the possibility to estimate the mineral quantity from XRD by using the relationship between the intensity of different minerals. The relative percentage of clay minerals was estimated by assuming that these minerals are present in an equal amount when $Sm(I)/It(I) - 3$, $Kt(I)/It(I) - 2$, and $Vt(I)/It(I) - 2$, where Sm(I), Kt(I), Vt(I) and It(I) represent the peak intensity for the respective clay mineral. The different mineral quantity of Kawazoe, Kubota and Isahaya clays are shown in Table 2. It can be seen that in all the three clays the predominant mineral is illite, more than 37% and smectite is of the order of 19% to 26% in clay size fraction unlike what has been reported widely in literature. From Table 2 it can also be seen that illite varies 18.9% to 25.6% and smectite varies from 11.5% to 15.1% in total soil fraction. It may be mentioned here that in the literature on Ariake clay invariably the intensity of peak is not presented at all.

In the light of the above findings, it is seen that the type and principal clay mineral percent in the overall soil fraction can vary widely in the clays of Ariake bay and each sample will require independent detailed examination if one wants to understand the mechanisms involved in the physico-chemical and physical behavior. The wide variations in the clay mineralogy (percent of different clay minerals) and percent clay size fraction are part of the reasons for the wide variation in their physical properties.

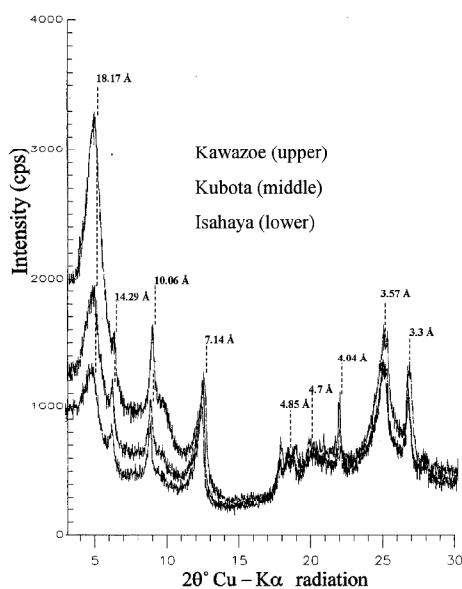


Fig. 3a XRD patterns of the Mg saturated glycerol solvated of Kawazoe, Kubota and Isahaya clays

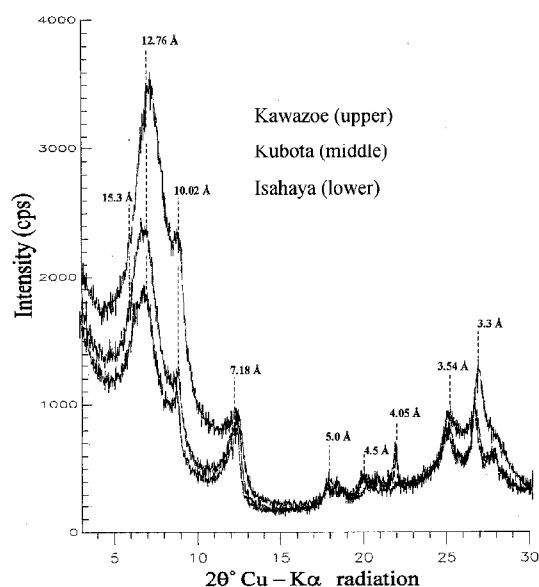


Fig. 3b XRD patterns of the K-saturated air-dried of Kawazoe, Kubota and Isahaya clays

Table 2 The distribution of clay minerals in Ariake clay in clay size and whole soil fraction

Ariake clays	Clay minerals in % in clay size fraction				Clay minerals in % in whole soil fraction			
	Smectite	Kaolinite	Vermiculite	Illite	Smectite	Kaolinite	Vermiculite	Illite
Kawazoe	26.1	15.4	20.0	38.5	15.1	9.2	11.5	22.3
Kubota	22.5	19.5	21.1	36.9	11.5	9.9	10.7	18.9
Isahaya	19.4	22.3	19.5	38.8	12.8	12.8	14.7	25.6

Table 3a presents the Atterberg limits of four different Ariake clays with wide variations in their liquid limits and the grain size distribution (Fig. 5). It is to be noted that although Kawazoe clay has 58.1% clay, its liquid limit (115.9%) is much less than Fukudomi ($w_L=134.4\%$) whose clay size fraction is only 49.9%. This is once again brings out that other parameters like pore medium chemistry consisting of different cations and their concentration can influence significantly the index properties. Table 3a also reports the Atterberg limits of samples initially oven dried before carrying out the index properties. The marked difference in the liquid limit, consequently on the plasticity index can be seen. The change in the plastic limit is not much. Figure 4 illustrates the effect of initial oven drying on the index properties in the plasticity chart. It may be seen that because of initial oven drying, the points moves down along the A-line and tend to wards below the A-line. Table 3b presents the results of Egashira and Ohtsubo (1981) on the effect of pre-test condition of the homoionized clays on the liquid limit. Even air-drying the soil brings down the liquid to an extent of 35%. The effect is more in calcium clays and when the concentration high, in Na clays also.

Table 3a Effect of pre-testing condition of Ariake clays on liquid and plastic limits.

Ariake clays	Liquid limit (%)		Plastic limit (%)		I_p		Percent Reduction in I_p
	Moist	Oven dried	Moist	Oven dried	Moist	Oven dried	
Kawazoe	115.9	68.6	45.5	34.1	70.4	34.5	51.0
Kubota	68.0	57.5	25.0	24.4	43.0	33.1	23.0
Isahaya	169.5	90.1	54.4	49.4	115.1	40.7	64.6
Fukudomi	134.4	86.6	45.0	42.4	89.4	44.2	50.6

Table 3b Effect of pre-testing condition of Ariake clay (Egashira and Ohtsubo 1981)

		Liquid limit (%)		Percent reduction in liquid limit
		Field moist	Air dried	
Na-Ariake clay:	0.01 N NaCl	89	79	11.2
	1.00 N NaCl	166	107	35.5
Ca- Ariake clay:	0.01 N CaCl ₂	151	107	29.1
	1.00 N CaCl ₂	168	109	35.1

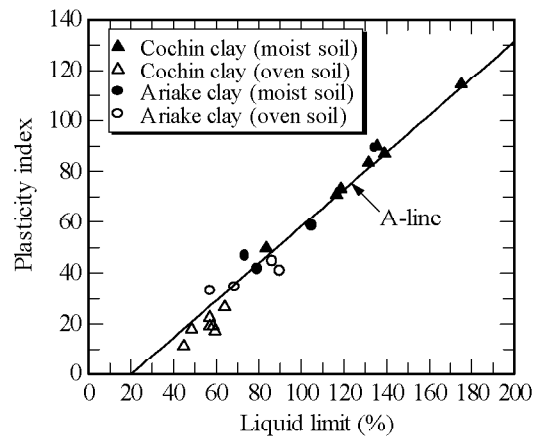


Fig. 4 Effect of pre-test condition on the liquid limit-plasticity index relationship

Figure 5 illustrates the effect of pre-test conditions on the grain size distribution of Ariake clays. It can be seen that the clay size fraction of Isahaya got reduced from 56% to 37%, for Fukudomi, the respective values are 50.5% and 23%. For Kawazoe clay the percent clay fraction got reduced from 48% to 21%. The reduction in percent clay fraction is quite significant. It may be mentioned that percent clay is an important parameter in the calculation of activity. Numbers of engineering properties have been related to activity.

Jose et al (1988b) have also reported the wide variations in the liquid limit and other index properties due to initial pre-test conditions of the Cochin marine clay. The variation in the liquid limit could be as high as 302% (Nettoor clay, Table 4) and it could be much higher in plasticity index. For Nettoor location of Cochin marine clay the plasticity index gets reduced from 90 to 11.2%. Even air-drying significantly influences the index and grain size distribution. Figure 6 shows typical grain size distribution of Cochin marine clay due to pre-test condition of the clays. Because of air-drying / oven drying aggregation of particles take place which is not reversible to a great extent (Jose et al. 1988b). Even soaking the oven-dried soil for a period of two months did not yield the liquid limit anyway nearer to the original moist value. These results bring out the importance of the pre-test condition of the marine clays and when results are reported it must be clearly mentioned that tests have been carried out with natural moist condition. Since the index property / consistency limits are widely correlated with engineering properties like C_c and S_u , utmost care is needed in getting the index properties of a marine clay. Rao et al. (1989) have reasoned out the reduction in liquid limit for initially oven dried south west Indian Cochin Marine clays. They brought out that the

Physical Properties of Ariake Clay

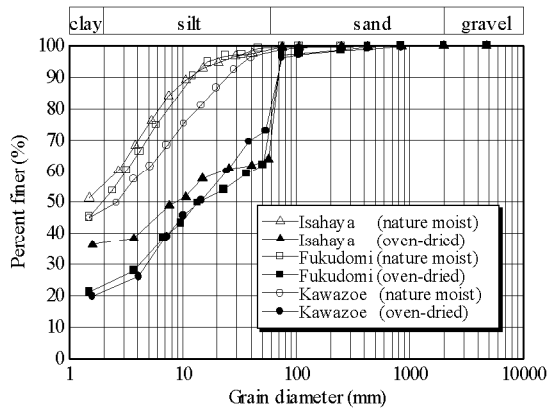


Fig. 5 Effect of pre-testing condition on the grain size distribution of Ariake clays

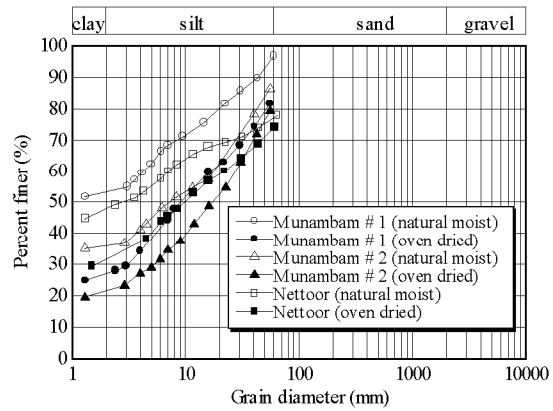


Fig. 6 Effect of pre-testing condition on the grain size distribution of Cochin marine clays

Table 4 Physical properties of Cochin marine clay (Jose et al. 1988b)

Site	Munambam			Nettoor		Cheranelloor	
Depth of sample (m)	9.4	10.4	12.1	1.0	1.5	2.0	5.5
1. Specific gravity	2.66	2.60	2.63	2.64	2.65	2.72	2.66
2. Bulk density (g/cc)	1.50	1.52	1.68	1.42	1.40	1.42	1.42
3. Natural Moisture content (%)	92.0	96.5	76.4	124.0	120.5	128.8	87
4. Liquid limit (%)							
(a) moist soil	116.5	139.0	83.5	135.5	131.5	175.0	118.5
(b) air dried	-	-	-	87.5	102.0	120.0	96.5
(c) oven dried	57.0	64.0	48.5	44.8	58.5	59.5	57.0
5. Plastic limit (%)							
(a) moist soil	45.5	52.0	33.8	47.5	48.0	60.6	45.3
(b) air dried	-	-	-	38.7	44.7	57.6	41.5
(c) oven dried	38.0	37.4	30.6	33.6	39.5	42.3	34.5
6. Plasticity index							
(a) moist soil	71.0	87.0	49.7	90.0	83.5	114.4	73.2
(b) air dried	-	-	-	48.8	57.3	62.4	55.0
(c) oven dried	19.0	26.6	17.9	11.2	19.0	17.2	22.5
7. Liquidity index	0.65	0.51	0.86	0.84	0.87	0.60	0.57
8. Shrinkage limit (%)							
(a) moist soil	22.5	23.1	23.2	17.8	17.0	18.1	19.3
(b) air dried	-	-	-	19.5	17.8	17.9	18.5
(c) oven dried	27.0	26.3	28.6	19.5	25	21.4	20.3
9. Grain size distribution							
(a) moist soil: (i) clay size (%)	42	54	35	48	47	45	36
(ii) silt size (%)	40	40	55	31	33	42	43
(iii) sand size (%)	18	6	10	21	20	13	21
(b) air dried: (i) clay size (%)	-	-	-	32	43	37	33
(ii) silt size (%)	-	-	-	43	35	48	46
(iii) sand size (%)	-	-	-	25	22	15	21
(c) oven dried: (i) clay size (%)	23	25	20	25	29	27	23
(ii) silt size (%)	59	65	70	48	48	58	56
(iii) sand size (%)	18	10	10	27	23	15	21
10. Activity: (a) moist soil	1.69	1.61	1.43	1.88	1.77	2.47	2.03
(b) air dried	-	-	-	1.53	1.36	1.68	1.67
(c) oven dried	0.83	1.04	0.90	0.44	0.69	0.63	1.0
11. Organic matter (%)	6.30	7.05	6.85	7.64	7.07	8.27	7.61
12. pH value	7.72	7.67	8.0	7.83	7.40	7.10	7.60
13. Calcium carbonate (%)	-	-	-	-	14.0	19.36	23.50
14. CEC (mcq/100 g)	-	37.7	-	26.0	-	36.0	-

presence of calcium and magnesium as the predominant exchangeable ions and of a high pore salt concentration facilitates strong inter particle attraction and small particle separations; the latter leads to development of significant capillary stresses that permits an intimate contact of particles and growth of strong van der Waals and Columbic bonds. The consequent aggregation of particles reduces the available surface for interaction with water and reduction in the liquid limit of the marine clay. Experimental verification of the above reasoning is seen from the results shown in Table 5.

Table 5 Effect of oven drying on the index properties of homoionized bentonites and montmorillonites (Rao et al 1989).

Serial Number	Clay type		Liquid limit (%)	Plastic limit (%)
1	Sodium bentonite	Moist	360	51.0
		Oven-dried	361	50.0
2	Calcium bentonite	Moist	145	44.9
		Oven-dried	117	30.5
3	Aluminum bentonite	Moist	137	72.1
		Oven-dried	66	44.5
4	Iron bentonite	Moist	133	79.0
		Oven-dried	86	58.7
5	Montmorillonitic black soil (India)	Natural water content	80	38.5
		Oven-dried	75	44.5
6	Montmorillonitic black soil treated with Al ³⁺ ions	Moist	67	50.9
		Oven-dried	45	34.6

In the light of the above discussion the results presented in Table 3b can be examined. With low concentration of 0.01 NaCl the difference between moist and air-dried is not much because repulsion is more under low concentration and Na is monovalent (Sridhara and Jayadeva 1982). The net attractive force is relatively less and hence aggregation is low. Between 0.01N of NaCl and 1.0 N of NaCl the difference in liquid is very high i.e. 166% and 107%. With higher concentration, the diffuse double layer repulsion is very less and hence net attraction is relatively high bringing the particle closer together upon air drying, aggregating them. Because of divalent Calcium in Ca Ariake clay, the repulsion is less and net attraction is more, aggregation takes place. Hence particles are bonded together well. Because of divalent Ca⁺⁺ ion, the effect of ion concentration is negligible unlike what has been noticed for Na⁺. The effect of ion concentration is quite high for Na ion. For Na clay under field moist condition the liquid limit gets increased from 89% to 166% and under air dried condition 79% to 107% due to increase ion concentration from 0.01 N to 1.0 N primarily because of increase in flocculation and in net attractive forces (Sridharan 1991).

ION CONCENTRATION

One of the important parameter that varies significantly in reclamation of marine clays are the type and concentration of ions. Egashira and Ohtsubo (1982) reports that variation of salt concentration with pore water of Yamaashi clay to be 0.10 to 0.85 g/l, Higashi-Shiroishi clay to vary 4.7 to 8.0 g/l, Ariake Kantaku clay to vary from 0.23 to 5.4 g/l. Ohtsubo et al. (1982) discussed the increase of ion concentration with depth from a value of 1.09 g/l (1 m depth) to up to about 10.4 g/l (5 m depth) and then a steady decrease to a level of 1.02 g/l (19m depth) for Higashi-Shiroishi clay. The primary types of cation content in clay are Na⁺, K⁺, Ca⁺⁺ and Mg⁺⁺ in order of their magnitude. In the Yamaashi profile the increase of ion concentration with depth is 0.25 g/l (2 m depth) to 1.08 g/l (7 m depth) and then decreasing with depth to a level of 0.05 g/l (17 m depth) with predominant cations being Na⁺, Mg⁺⁺, Ca⁺⁺ and K⁺. The

Megurie clay of Ariake contains ion concentration decreasing with depth from about 28 g/l to about 0.87 g/l (at a depth of 20 m). The Okishin clay of Ariake bay has concentration varying from 32.7 g/l to 1.5 g/l with depth 1m to about 40m (Ohtsubo et al. 1983). The Megurie Kantaku clay is reported to have a salinity of 23.5 g/l (Torrance 1984). The Megurie (E-17) sample and the Kawazoe (W-179-3) sample of Ariake clays have salt content of 13.5 g/l and 0.5 g/l, respectively (Ohtsubo et al. 1985).

Torrance and Ohtsubo (1995) reported in detail the variation of salinity of four sites in Ariake bay with depth. For Okishin clay the salinity decreases from 34.7 g/l at a depth of 5 m to 1.5 g/l at a depth of 44 m; for Higashi-Shiroishi the salinity first increases from 1.1 g/l (2 m depth) to 10.4 g/l (6 m depth) then steadily decreases to 1.0 g/l at depth of 19 m. For Yamaashi profile the salinity increases 0.3 g/l (2 m depth) to 1.55 g/l (8 m depth) and then steadily decreases to 0.16 g/l (17 m depth). Significant erratic variations in ion concentration 4.0 g/l to 20.1 g/l with depth have been noticed for the Ariake clay from Ariake town, Saga prefecture (Ohtsubo et al. 1995). Results like the above and other results clearly indicate that the ion concentration varies significantly for the Ariake clays and it could be as high as 34.7 g/l and to a very low level of negligible quantity. It is generally increases marginally with depth then decreases significantly with depth. The main cation present in the pore medium is Na and the other cations are Mg^{++} , Ca^{++} and K^{+} in order of their magnitude. The magnitude of ion concentration and the type of ion in marine clays varies significantly depending upon the geological and other factors (Ohtsubo et al. 1995; Ohtsubo et al. 1996).

EFFECT OF PORE MEDIUM CHEMISTRY ON LIQUID LIMIT

There is an overwhelming results show that the liquid limit of clays is governed by two distinct mechanisms (Sridharan and Rao 1975; Sridharan et al. 1986; Sridharan et al. 1988) depending upon the predominant clay mineral is montmorillonite (swelling) or kaolinite (non swelling). For montmorillonitic soils the contribution of diffuse double layer water to the liquid limit dominates. In other words factors, which facilitates to increase the diffuse double layer thickness like reduction in ion concentration, decrease in the valence of ion in the pore water and increase in the dielectric constant of the pore medium increases the liquid limit of montmorillonitic or swelling soils. For kaolinitic/non swelling soils fabric towards flocculation and the net increase in the electrical attractive force at particle level increasing the shearing resistance increases the liquid limit. It is long been recognized that various types of fabric can be formed in a clay-electrolyte system. van Olphen (1964) opines that where the attractive force is large and repulsive force is small kaolinite particles will associate with each other in an edge-to face manner (flocculated). An open flocculated structure has greater shear strength and water holding capacity (larger liquid limit). In other words factors which facilitates flocculent or open fabric, viz. increase in ion concentration and /or ion valence of the pore medium and a decrease in the dielectric constant resulting in increase net attractive force at particle level leads to higher water holding capacity or liquid limit.

Table 6a and 6b present the dominating mechanisms and some results. In Table 6, the significant effect of variation in the pore medium chemistry primarily represented by (i) ion concentration, (ii) valence of cation, (iii) dielectric constant of the pore fluid, and (iv) hydrated size of the ion on the liquid limits of montmorillonitic (swelling) and kaolinitic soils grouping them as per the dominating mechanism controlling the behavior. It may be seen that the behavior between these two groups of soils is quite opposite. It is seen for montmorillonite in Table 6a that the effect of (i) decrease in dielectric constant is to decrease the liquid limit to the extent of 83% when the fluid is changed from water to heptane, (ii) increase in ion concentration is to decrease to the extent of 60% when the concentration is increased from 0.01 NaCl to 1.0 NaCl, (iii) increase in valence is to decrease to the extent of 75% to 82% when

Na^+ is changed to Ca^{++} , and (iv) decrease in hydrated size of the ion is to decrease the liquid limit the extent of about 65% when Li^+ is changed to K^+ .

For kaolinite (Table 6b), the effect of (i) decrease of dielectric constant on liquid limit is to increase it to the extent of 81% when water is changed to hexane, and (ii) increase of ion valence from Na to Ca is to increase the liquid limit by about 40%. For Kundara clay (kaolinitic soil), the effect of increase of concentration from nil to 0.5 N NaCl is to increase the liquid limit by about 45%. For illite (Table 6b) the effect of increase of valence 1 to 2 (Na to Ca) increases the liquid limit by about 48%. Thus it is seen the mechanisms controlling the liquid limit oppose each other and the effect of pore medium chemistry could be very significant. Table 7 summarizes the effect of pore medium chemistry on the liquid limit of swelling (montmorillonitic) and non-swelling (kaolinitic) clays based on the results reported in Table 6. In natural clays as against the pure system, several clay minerals are present with multivalent ion and with different concentrations exist. Hence both the mechanisms as discussed above co-exist but one of them dominates. Depending upon the dominating mechanism the final behavior is seen.

Table 6a Diffuse double layer dominating the overall behavior and controlling the value of the liquid limit

I	Description of sample	Liquid limit (%)	Reference
Na-Montmorillonite:	Water	950	Yong & Warkentin (1975)
	0.01 N NaCl	870	-do-
	1.00 N NaCl	350	-do-
Ca-Montmorillonite:	Water	360	-do-
	1.00 N CaCl_2	310	-do-
Bentonite:	Water as fluid	332	Sridharan & Prakash (1999)
	0.5 N NaCl solution	94	-do-
	CCl_4 as fluid	54	-do-
Black cotton soil:(montmorillonitic soil):	Water as fluid	92	-do-
	0.5 N NaCl solution	85	-do-
	CCl_4 as fluid	45	-do-
Na-Montmorillonite		700	White (1949)
Ca-Montmorillonite		177	-do-
Na-Bentonite		410	Rao et al. (1993)
Seawater equilibrated bentonite		142	-do-
Li^+ -Bentonite (7.3 -10.0)*		675	Sridharan, Rao & Murthy (1986)
Na^+ -Bentonite (5.6 - 7.9)		495	-do-
NH_4^+ -Bentonite (5.4)		223	-do-
K^+ -Bentonite (3.8 - 5.3)		233	-do-
Mg^{++} -Bentonite (10.8)		129	-do-
Ca^{++} -Bentonite (9.5)		125	-do-
Ba^{++} -Bentonite (8.8)		108	-do-
Al^{+++} -Bentonite		108	-do-
II	Soil: Montmorillonite	(Sridharan and Rao 1975; Sridharan 1991)	
	Fluid type	Dielectric constant	Liquid limit (%)
			Weight basis**
			Volume basis
	Hexane	1.89	52.8
	Heptane	1.92	51.5
	Carbon tetra chloride	2.28	54.7
	Ethyl Acetate	6.02	63.8
	Acetone	20.70	72.5
	Ethanol	24.30	70.7
	Methanol	32.63	75.6
	Water	80.40	306.0
			866.0

*Values in the parentheses gives the hydrated size of cations in Angstrom units (Mitchell 1993).

**Normalized for the density of the fluid.

Table 6b Flocculation and/or increase of attractive force dominating the overall behavior and controlling the value of the liquid limit.

I	Description of sample	Liquid limit (%)	Reference
	Na-Kaolinite	52	White (1949)
	Ca-Kaolinite	73	-do-
	Na-Illite	61	Yong & Warkentin (1975)
	Ca-Illite	90	-do-
	Na-Kaolinite: 0.01 N NaCl	34	-do-
	1.00 N NaCl	40	-do-
	Kaolinite Water as fluid	49	Sridharan & Prakash (1999)
	CCl ₄ as fluid	81	-do-
	Kundara clay (Kaolinitic soil) Water as fluid	38	-do-
	0.5 N NaCl solution	55	-do-
	CCl ₄ as fluid	73	-do-
II	Soil: Kaolinite	(Sridharan and Rao 1975; Sridharan 1991)	
	Fluid type	Dielectric constant	Liquid limit (%)
			Weight basis* Volume basis
	Hexane	1.89	88.9 230.0
	Heptane	1.92	86.0 231.0
	Carbon tetra chloride	2.28	88.3 228.5
	Ethyl Acetate	6.02	75.4 195.2
	Acetone	20.70	78.2 202.2
	Ethanol	24.30	73.1 189.2
	Methanol	32.63	64.5 167.0
	Water	80.40	49.0 127.0

*Normalized for the density of the fluid

Table 7 Summary of liquid limit behavior

Increase in	Liquid limit	
	Kaolinitic/non swelling soil	Montmorillonitic/swelling soil
Dielectric constant	Decrease	Increase
Concentration of ions in pore medium	Increase	Decrease
Hydrated size of ions in pore medium	Decrease	Increase
Valence of cation	Increase	Decrease

Figures 7a, b, c, and d bring out the effect of ion concentration on the liquid limit of clays. Figure 7a illustrates (i) Sodium equilibrated bentonite, curve a (results of Rao et al. 1993). (ii) Artificial seawater equilibrated bentonite- curve b (results of Rao et al. 1993) and Megurie-Ariake clay, (1.5m depth) curve c (Ohtsubo et al. 1996).

At first instance, these three clays are compared. Curve a in Fig. 7a is for bentonite clay equilibrated with 40 g/l of sodium chloride solution for a period of 90 days and subsequently leached to lower salinity. The liquid limit of bentonite (curve a) primarily depends upon the diffuse double layer water surrounding the particles. A decrease in the pore salt concentration enhances the amount of diffuse double layer water and hence increases the liquid limit of swelling clays through out. The results are supported by mechanism presented earlier and the results in Table 6a and Table 7.

Curve b shows the pore salt leaching on the liquid limit behavior of bentonite clay exposed to artificial seawater for a period of 1 year (Rao et al. 1993). Artificial seawater equilibrated bentonite for a period of one year was subsequently leached gradually. The composition of the artificial seawater as per ASTM (1976) Specification is given in Table 8. Artificial seawater contains 9.66 g/l of dissolved sodium ions, 1.33 g/l of magnesium, 0.42 g/l of calcium and 0.40 g/l of potassium (data from Table 8). The time required to reduce the pore salinity of the bentonite-seawater suspension at each stage of leaching ranged from 2 days to 10 days.

Table 9 present pore water cation concentration in the suspension extract of 1-year seawater equilibrated bentonite specimens at various stages of leaching (Rao et al. 1993) together with the respective liquid limit. It has further been reported by Rao et al. (1993) that the bentonite clay mineral is same in both the clays and does not undergo any mineralogical changes due to treatment of artificial seawater. Unlike what has been noticed for bentonite equilibrated with monovalent Na ion, (curve a) the liquid limit increases with reduction in concentration to an optimal level and then get decreased. The predominant decrease in the level of liquid limit between Na ion alone and that of multi ions present in the artificial seawater is evident below the salt concentration level of pore water of 9 g/l. It is further interesting to note that the liquid limit of artificial seawater equilibrated bentonite is more than that of sodium chloride equilibrated bentonite beyond a concentration level of 9 g/l, which shows the occurrence of flocculation when higher valence ion exists in the pore water. The lesser value of liquid limit of 'curve b' when compared with 'curve a' below a concentration level of 9 g/l is attributed to the depressed double layer because of higher valence ions in the artificial seawater (Sridharan and Jayadeva 1982). Below the concentration level of 9 g/l, the bentonite treated with artificial seawater (curve b) increases in its liquid limit as concentration decreases, reaches an optimal level when the concentration is 1.05 g/l (see Table 9 and Fig. 7) and then decreases.

As discussed earlier, that as concentration increases, especially so when higher valence ions present, simultaneously two phenomena take place: (i) the diffuse double layer water gets depressed leading to decrease in the liquid limit and (ii) flocculation of clay platelets take place together with the increase in electrical attractive force mainly contributed by the columbic and van der Waals forces between particles increase leading to increase in the liquid limit. While both phenomena takes place simultaneity one of them dominates. In the case of bentonite treated with artificial sea water and subsequent leaching, gradually flocculation of particles takes place as concentration of ions gets increased leading to larger entrapment of water and hence higher liquid limit up to a concentration level of 1.05 g/l and beyond that diffuse double layer mechanism dominates leading to decrease in the liquid limit.

In the light of the behavior of bentonite treated with two different systems (curve a and b of Fig. 7a) one can examine the Ariake clay behavior. It is strikingly clear that as the concentration increases (curve c) the liquid limit significantly increases up to an optimal level and further a decreasing trend is seen. Once again the same reasoning of bentonite clay treated with artificial seawater and subsequently leached (curve b, Fig. 7a) holds good. It may be seen that up to the higher concentration level to which the results are available the liquid limit increases with increase in concentration reaching an optimum level and then a slight decrease is seen. In a natural soil, different clay minerals are present and the ion type and its concentration varies as the leaching takes place. Though the system is complex, the trend of the behavior and the mechanisms controlling them are fairly clear.

Figure 7b presents the effect of cation valence and ion concentration on the liquid limit. Increase of cation valence and concentration increases the flocculation and attractive forces leading to increase in the liquid limit. When the ion concentration is very low, the divalent cation Ca^{++} promotes larger attraction and flocculation when compared to Na^+ , leading to large difference in liquid limit almost 100% increase. The effect of divalent Ca^{++} ion is two fold: (i) to depress the diffuse double layer and (ii) to increase the attractive force at particle level and increase the flocculation. The effect of the above two phenomena on liquid limit is to oppose each other. The end result is that one of the mechanisms dominates over shadowing the other phenomena. At high concentration level, diffuse double layer is depressed substantially; net attraction gets increased for both Na and Ca clays resulting in almost same value of liquid limit. The depression of diffuse double layer with increase in concentration gets completely over shadowed the increase in flocculation increasing the liquid limit. The effect of cation valence gets masked due to high ion concentration and both Na and Ca clays yields almost same

value of liquid limit.

Figure 7c illustrates the effect of ion concentration on six Ariake clays from different locations. In spite of variation in clay size fraction, different percentage of different clay minerals and different types of ions and their concentration a good trend in their behavior is seen. It may be mentioned here that the primary cation in the marine clays of Ariake clay is Na. This has been overwhelmingly established (e.g. Ohtsubo et al. 1982). The primary cation in sea-water is also Na (Table 8). In view of this, the Na clay of Ariake has also been included in Figure 7c.

Considering the various parameters involved in the complex system there is a good trend in the behavior-concentration being the primary parameter. The dominating mechanism i.e. either diffuse double layer water contributing to the increase/decrease of liquid limit with decrease/increase of concentration respectively or the open fabric created by increased electrical attractive forces due to concentration increase and/or increase in the valence

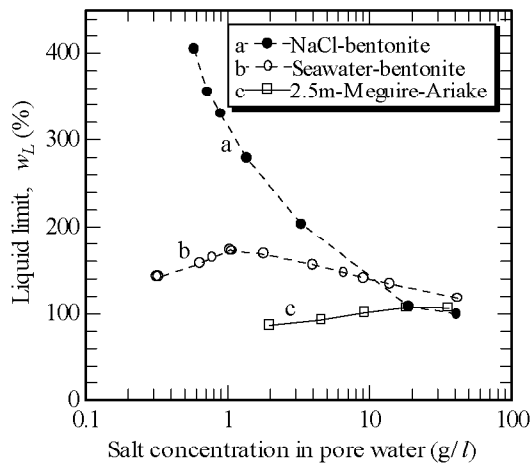


Fig. 7a Effect of salt concentration in pore water on the liquid limit

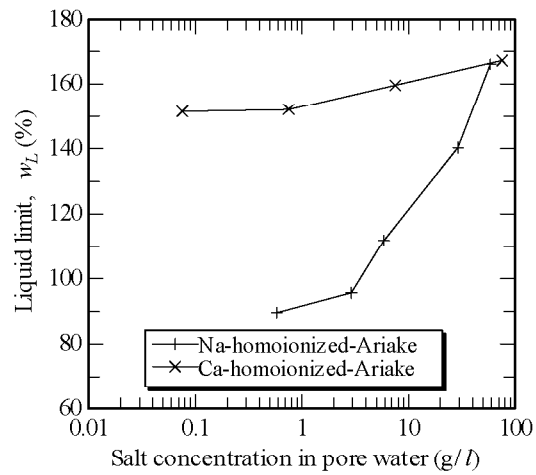


Fig. 7b Effect of salt concentration in pore water on liquid limit of homoionized Ariake clay

Table 8. Composition of the artificial seawater as per ASTM (1976) specification

Name	Electrolyte formula	Electrolyte concentration (g/l)	Concentrations of major cations present (g/l)
Sodium chloride	NaCl	24.53	9.66
Magnesium chloride	MgCl ₂	11.11	1.33
Sodium sulfate	Na ₂ SO ₄	4.10	1.31
Calcium chloride	CaCl ₂ (anhydrous)	1.16	0.42
Potassium chloride	KCl	0.70	0.40
Sodium bicarbonate	NaHCO ₃	0.20	-
Potassium bromide	KBr	0.10	-
Strontium chloride	SrCl ₂ · H ₂ O	0.04	-
Boric acid	H ₃ BO ₃	0.03	-
Sodium fluoride	NaF	0.01	-
Barium nitrate	Ba(NO ₃) ₂	9.94 × 10 ⁻⁵	-
Manganese nitrate	Mn(NO ₃) ₂ · 6H ₂ O	5.46 × 10 ⁻⁵	-
Copper nitrate	Cu(NO ₃) ₂ · 3H ₂ O	3.96 × 10 ⁻⁵	-
Zinc nitrate	Zn(NO ₃) ₂ · 6H ₂ O	1.51 × 10 ⁻⁵	-
Lead nitrate	Pb(NO ₃) ₂	6.6 × 10 ⁻⁶	-
Silver nitrate	AgNO ₃	4.9 × 10 ⁻⁷	-

resulting in higher entrapment of water contributing to the increase in the liquid limit depends on the type of clay minerals present with their relative proportion in the clay size fraction, the percent non clay size fraction and the pore medium chemistry primarily represented by the cation concentration and the valence of different cations present. When the valence and concentration are same, the hydrated size of the cation can bring in differences in the liquid limit, Table 6a (Sridharan et al. 1986).

Figure 7d is a replot the results presented in Fig. 7c. One can see a very good correlation between salt concentration in pore water and liquid limit for Ariake clays. A statistical fit gives $w_L = 97.1 C^{0.0866}$ with a correlation coefficient $R^2 = 0.99$.

Table 9 Pore water cation concentration in the suspension extracts of 1-year seawater-equilibrated bentonite specimens at various stages of leaching (Rao et al. 1993)

Leaching stage	Salt concentration of the suspension extract from conductance measurement (g/l)	Liquid limit (%)	Dissolved Ion concentration in the pore water (g/l)			
			Ca	Mg	Na	K
-	41.6	118	0.35	1.09	12.63	0.31
1	14.0	134	0.16	0.43	6.85	0.17
2	9.0	141	0.11	0.31	4.50	0.12
3	6.6	147	0.08	0.22	3.10	0.08
4	4.0	156	0.07	0.19	2.70	0.07
5	1.80	168	0.03	0.06	0.80	0.03
6	1.08	172	0.01	0.03	0.50	0.03
7	1.05	173	0.01	0.03	0.45	0.02
8	0.78	164	0.01	0.02	0.40	0.02
9	0.64	157	0.01	0.02	0.35	0.01
10	0.33	142	0.01	0.01	0.25	0.01
11	0.32	142	0.01	0.01	0.22	0.01

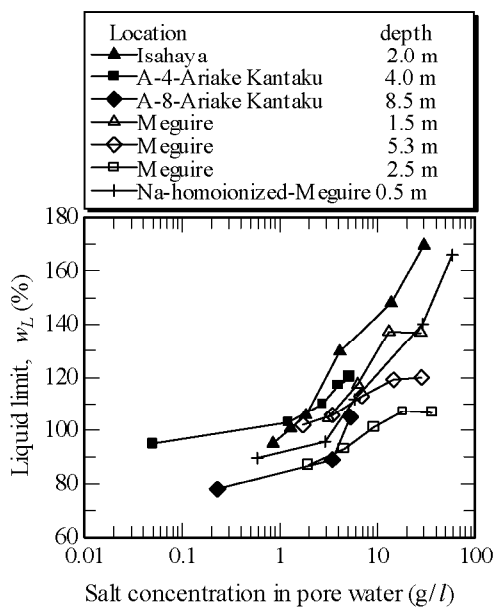


Fig. 7c Effect of salt concentration in pore water on liquid limit of Ariake clays.

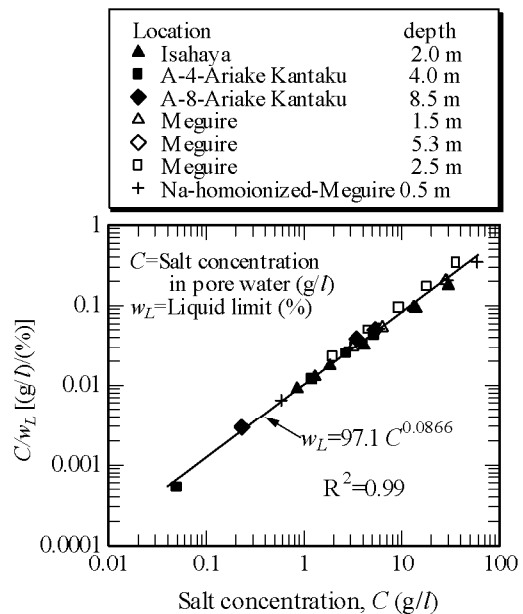


Fig. 7d Liquid limit vs. salt concentration in pore water relationship

CONCLUSIONS

Considering many marine clays of the world, the variation in physical and engineering properties are very high for Ariake clay. It has been reasoned out that Ariake clay contains smectite, illite, kaolinite, and vermiculite as primary clay minerals. Many studies have shown that smectite as principal clay mineral. Further detailed investigation has revealed that illite could also be the principal clay mineral. Depending upon the geological history and other depositional conditions the type of clay mineral and magnitude of the same can vary to a great extent. Since in many Ariake clays non-clay fraction is quite substantial, the percentage of different clay minerals gets vastly reduced and also varied. For example for Kubota clay the smectite content can reduce 22.5% to 11.5% and illite content can reduce 36.9% to 18.9%. This is one of the aspects, which is responsible for wide variations in the physical properties.

Pore medium chemistry is another important factor. The ion concentration can vary widely in Ariake clays (0.04 g/l to nearly 40 g/l) and the principal ions are Na, Ca, Mg, and K in order of their magnitude. Comparison of Ariake clay with change in ion concentration has been examined with bentonite treated with artificial seawater and it has been found that two dominating mechanisms control their liquid limit behavior. As concentration and /or ion valence increases, flocculation can take place leading to increase in liquid limit. At the same time the diffuse double layer gets depressed decreasing the liquid limit. Thus it is seen that these two mechanisms oppose each other. However both mechanisms co-exist, and depending upon the factors like relative proportion of various clay minerals, percent clay size fraction and type and concentration of various ions one of the mechanisms dominates.

For Ariake clay it is clearly seen that as concentration increases net electrical attractive force increases leading to flocculation, leading to increase in liquid limit up to an optimum level of concentration. Beyond this concentration level, the diffuse double layer gets depressed significantly, leading to reduction in liquid limit. Since in Ariake clay all the important parameters viz. type of clay mineral, percent clay size fraction, ion concentration and different types of ion varies, the system is a complex one. In spite of this the variation in liquid limit with ion concentration is within a narrow band (Fig. 7c and 7d) for various Ariake clays examined with wide variation in their clay minerals, percent clay size fraction and pore medium chemistry.

Pre-test condition of soil (either natural moist/ air dried/ oven dried) has significant influence on the physical properties of Ariake clay. It is utmost important that care should be taken to test them in natural moist condition in view of the importance of physical properties in geotechnical engineering practice.

REFERENCES

- American Society for Testing and Materials (1976). Standard specification for substitute ocean water; ASTM designation D1141-75. Annual Book of (ASTM), Part31, Philadelphia.
- Egashira, K. and Ohtsubo, M. (1981). Low swelling smectite in a recent marine mud of Ariake bay. *Soil Sci. Plant Nutr.* 27(2):205-280.
- Egashira, K. and Ohtsubo, M. (1982). Smectite in marine quick clays of Japan. *Clays and Clay Minerals.* 30: 275-280.
- Hong, Z. and Tsuchida, T. (1999). On Compression characteristics of Ariake clays. *Canadian geotechnical J.* 36:807-814.
- Jose, B.T., Sridharan, A. and Abraham, B.M. (1988a). Physical properties of Cochin marine clays. *Indian Geotechnical J.* 18(3): 226-244.
- Jose, B.T., Sridharan, A. and Abraham, B.M. (1988b). A study of geotechnical properties of Cochin marine clays. *Marine Geotechnology.* 7: 189-209.

- Miura, N., Akamine, T. and Shimoyama, S. (1996). Study on depositional environment of Ariake clay formation and its sensitivity. *J. Jpn. Soc. Geotech. Engrg.* 541(III-35): 119-131
- Ohtsubo, M., Takayama, M. and Egashira, K. (1982). Marine quick clays from Ariake Bay area, Japan. *Soils and Foundations.* 22(4): 71-80.
- Ohtsubo, M., Takayama, M. and Egashira, K. (1983). Relationships of consistency limits and activity to some physical and chemical properties of Ariake marine clays. *Soils and Foundations.* 23(1): 38-46.
- Ohtsubo, M., Egashira, K. and Takayama, M. (1985). Properties of a low swelling marine clay of interest in soil engineering. *Canadian geotechnical J.* 22: 241-245.
- Ohtsubo, M., Egashira, K. and Kashima, K. (1995). Depositional and post-depositional geochemistry, and its correlation with the geotechnical properties of marine clays in Ariake Bay, Japan. *Geotechnique.* 45: 509-523.
- Ohtsubo, M., Egashira, K. and Takayama, M. (1996). Mineralogy and chemistry, and their correlations with the geotechnical properties of marine clays in Ariake bay, Japan: Comparison of quick and nonquick clay sediments. *Marine Georesources and Geotechnology.* 14: 263-282.
- Ohtsubo, M., Egashira, K., Koumoto, T. and Bergado, D.T. (2000). Mineralogy and chemistry, and their correlation with the geotechnical index properties of Bangkok clay: comparison with Ariake clay. *Soils and Foundations.* 40(1): 11-21.
- Rao, B.M. (1974). Geotechnical investigation of the marine deposits in the Mangalore harbour site. *Indian Geotechnical J.* 4: 78-92.
- Rao, S.M., Sridharan, A. and Chandrakaran, S. (1989). Influence of drying on the liquid limit behavior of a marine clay. *Geotechnique.* 39(4): 715-719.
- Rao, S.M., Sridharan, A. and Chandrakaran, S. (1991). Engineering behaviour of uplifted smectite-rich Cochin and Mangalore marine clays. *Marine Geotechnology.* 9(4): 243-259.
- Rao, S.M., Sridharan, A. and Chandrakarn, S. (1993). Consistency Behavior of Bentonites exposed to sea water. *Marine Georesources and Geotechnology.* 11: 213-227.
- Sridharan, A. and Rao, G.V. (1975). Mechanisms controlling the liquid limit of clays. *Proc. Istanbul Conf. on SM and F.E.* 1: 65-74.
- Sridharan, A. and Jayadeva, M.S. (1982). Double layer theory and compressibility of clays. *Geotechnique,* 32(2): 133-144.
- Sridharan, A., Rao, S.M. and Murthy, N.S. (1986). Compressibility behaviour of homoionized bentonites. *Geotechnique.* 36(4): 551-564.
- Sridharan, A., Rao, S.M. and Murthy, N.S. (1988). Liquid limit of kaolinitic soils. *Geotechnique,* 38(2): 191-198.
- Sridharan, A. (1991). Engineering Behavior of Fine Grained Soils,-A Fundamental Approach. *Indian Geotechnical J.* 21(1):1-136.
- Sridharan, A. (1999). Engineering behaviour of Marine clays. *Geo Shore, Int. Conf. on off Shore and Near Shore Geot. Eng. Bombay.* Oxford and IBH Publishing, New Delhi: 49-64.
- Torrance, J.K. (1975). On the role of chemistry in the development and behavior of sensitive marine clays of Canada and Scandinavia. *Canadian Geotechnical J.* 12: 326-335.
- Torrance, J.K. (1984). A comparison of marine clays from Ariake Bay, Japan and the South Nation River landslide site, Canada. *Soils and Foundations.* 24: 75-81.
- Torrance, J.K. and Ohtsubo, M. (1995). Ariake Bay quick clays: a comparison with general model. *Soils and Foundations.* 35(1): 11-19.
- Van Olphen. H. (1963). *An Introduction to Clay Colloid Chemistry.* John Wiley, New York.
- Wada, K. (1966). Qualitative and Quantitive Determinations of Clay Minerals. *Journal of the Science of Soil and Manure, Japan., Plant and Fertilizer.* (Special Issue). 37(1): 9-17.
- Whittig, L.D. and Allardice, W.R. (1986). X-Ray Diffraction Techniques. *Methods of Soil Analysis,* 2nd ed. American Society of Agronomy-Soil Science: 331-362.