Pore Structure Analysis of a Silt with Additives

by

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Introduction

The specific surface area of a porous solid and the pore volume distribution as a function of pore sizes have become progressively more important in understanding the chemical and physical behaviour of porous materials. These characteristics have long been recognized as important in the assessment of the chemical activity of catalysts. Of late, the importance of pore size distribution (PSD) data in understanding soil behaviour is being increasingly recognised. Soil structure has long been recognized as important in the field of soil mechanics. Considerations involving many of the elements of soil structure have been useful in explaining soil behaviour. The importance of one of these-the void ratio-in compressibility and strength behaviour is common knowledge. In the past, the understanding of the soil behaviour was from the void ratio point of view (which is a total pore volume parameter) and little attention was paid to the significance of the pore sizes by themselves. The PSD in soils has a great bearing on the three important inter-related engineering properties of soils, viz.; strength, compressibility and permeability and also the susceptibility of soils to frost action. Several methods (Childs and Collis-George, 1950; Marshal, 1958; Millington and Ouirk, 1959) have been proposed, by which permeability may be calculated from PSD. The importance of PSD in permeability has been well brought out by Olsen (1962). Klock et al (1969) measured permeabilities and pore size distributions of various sizes of glass beads and sand, and found that after the use of a correction factor there was good agreement between the calculated and measured values of permeabilities. Sridharan (1968) and later Venkatappa Rao (1972) computed the negative pore water pressure from PSD and explained the experimentally observed strength behaviour of various clays in the partly saturated condition (Venkatappa Rao and Sridharan, 1978).

PSD in soils is affected by a wide variety of factors; it can vary to a great extent between two soils even though they may have essentially the same particle size distribution. Even for a particular soil, the PSD can vary over wide limits depending upon the particle arrangement which for a natural soil deposit or a compacted soil, depends upon a number of factors (Sridharan *et al* 1971). Changes in the PSD arising from mechanical loading, remoulding, chemical treatment, plant root growth, freezing and

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This paper was received in February 1979 and is open for discussion till the end of March 1980.

thawing, or other influences often need to be taken into account in interpreting the experimental results. Recently Esmer *et al* (1969) studied the effects of lime stabilization and freezing and thawing on the soil pore structure and permeability of fine grained soils. In the present study the effect of addition of lime and/or fly ash on the pore structure of an alluvial silt is studied in detail.

Two independent methods exist for pore size distribution analysis. The first, the mercury injection method, is based on the concept of forced intrusion of a non-wetting liquid into the pores under pressure and was suggested by Washburn in 1921 and was later fully developed by Ritter and Drake (1945). A significant advance in soil structure studies was made by Sridharan (1968) and Sridharan et al (1971) who demonstrated that mercury injection porosimetry can be used to characterize PSD of soils and to provide a better understanding of engineering modifications of soil such The major limitation of mercury porosimetry is the as compaction. difficulty involved in measuring sizes of fine pores because of the requirement of high pressures for e.g., a pressure of 1,400 kg/cm² is required to measure about 90° A° of pore diameter. At such pressure crushing and distortion are of concern. The second method of PSD analysis, the sorption (isotherm) method, invokes the concept of capillary condensation in the pores. Analysis of sorption isotherms has been extensively used to study the pore structure of various materials. Most of the methods developed during the past 25 years make use of Kelvin's capillary condensation equation and Brunauer, Emmett and Teller's (1948) multi-layer adsorption theory. Sridharan and Venkatappa Rao (1975a, 1975b) studied the PSD of various soils by the analysis of sorption isotherms using Brunauer's Modelless method, developed recently. Pore size distribution curves obtained from the adsorption isotherm are compatible with mercury porosimetry results (Huang and Demirel, 1973). The two methods of measuring pore volume and distribution, when used jointly permit measurement of the complete pore spectrum.

Pore Size Distribution by Analysis of Water Vapour Sorption Isotherms

Various investigators have advanced methods of analysing the sorption isotherms for the pore structure determination (e.g., Cranston and Inkley, 1957; Roberts, 1967; Brunauer *et al*, 1967*a*). The analysis of pore shapes and sizes from the vapour sorption isotherm involves three important steps.

- (i) Reduction of the actual shape of pores present in the adsorbent to restricted number of idealised shapes, *i.e.* cylindrical spheroidal or slit-like pores.
- (ii) Identification of the sorbed phase with capillary retained bulk liquid.
- (iii) Application of Kelvin's equation (or a similar equation) to the bulk liquid present in (supposedly) ideal pore shapes.

In the above, each step involves severe simplification of physical reality and it cannot be expected that the conclusions drawn from a pore size and pore shape analysis would be strictly valid. Nevertheless, in a number of instances the results of such an analysis have yielded valuable information on pore sizes and shapes, fairly consistent with information from other sources such as crystallography and electron microscopy, (Broekhoff and Linsen, 1970). All previous investigators (except Brunauer and co-workers, 1967*a*) employed some pore shape model in their analysis of pore volume and surface distributions. The cylindrical model has been by far the most widely employed. The reason for this is that, Kelvin's equation which gives the pore radius that is desorbed at known partial pressure has a simple form. Brunauer *et al* (1967*a*) published a modelless method for pore structure analysis. It is modelless, in the sense that it assumes no shape for pores. The analysis is based on the hysteresis region of the sorption isotherms. The pore volume and surface distributions are determined as functions of hydraulic radii. To quote Brunauer (1967*b*):

"The great superiority of this method over the presently employed cylindrical or parallel plate idealizations is that the present idealizations are based on one value obtained from the isotherm, the volume of the core (volume desorbed) but the hydraulic radii and the surface area are hypothetical; whereas the new method is based on two values obtained from isotherm—the volume and the surface of the core, which automatically give the hydraulic radius of the core".

For the reasons stated above as to the superiority of this method over others, this method has been presently used to obtain pore size distribution in soil—lime—fly ash admixtures. An outline of the Brunauer's method is given below.

The pore volume and surface distributions, are determined as functions of hydraulic radii in this method by Brunauer *et al* (1967*a*). The hydraulic radius for a pore or a group of pores is defined as

$$r_h = \frac{V}{S} \qquad \dots (1)$$

where V = Volume of pore or pore system

S = Surface area of pore walls.

This definition applies to pores of any shape. For a cylindrical pore, r_h is equal to half of the radius of the cylinder; for a parallel plate pore, it equals half the distance between the plates.

The values of V and S are obtained from adsorption or desorption isotherms as follows. When the relative pressure (P/P_s) is lowered, for e.g. from 1.0-0.95, a group of pores empty by capillary evaporation. The pores do not empty completely; a multilayer of adsorbed film still remains on the walls. The part of the pore space which is empty is called the core. The volume of the core is the volume desorbed between $P/P_s = 1.0$ and 0.95. The surface area of the core can be determined by means of Kieslev's equation (Brunauer, 1967a) given by

$$S = -\frac{1}{\gamma} \int_{a_H}^{a_s} R T \ln P/P_s \ da \qquad \dots (2)$$

 $\gamma =$ Surface tension of the adsorbate, viz. water in the present

where,

case. R = gas constant

T =temperature in °K

 $P/P_s =$ relative pressure

- da = surface that disappears when a pore is filled by capillary condensation
- $a_s =$ number of moles adsorbed at saturation, and
- a_H = number of moles adsorbed at the beginning of the hysteresis loop.

Kelvin's equation is a special case of the Kieslev's equation.

Now, hydraulic radius of the core is V/S.

When P/P_s is lowered from 0.95 to 0.50, the volume desorbed (a_2) is not the volume of the cores of the second group. There is an adsorbed film on the pore walls of the first group at $P/P_s = 0.95$, and some of this adsorbate desorbs when the relative pressure is lowered to 0.90, (let this be V'_2). Hence the volume of the cores of the second group is $(a_2-V'_2)$. From Kieslev's equation, the area of the cores of this group can be obtained by integrating Equation 2 from the volume adsorbed at $P/P_s = 0.95$ to the volume adsorbed at $P/P_s = 0.90$ less V'_2 and hence the hydraulic radius.

The determination of the core volumes, surfaces, and hydraulic radii for the subsequent groups of pores are performed in a similar manner. The method was discussed above for a desorption isotherm, but it is equally applicable for adsorption isotherms.

The correction terms discussed before are calculated on the basis of a *t*-curve. The *t*-curve is a plot of the statistical thickness of the film adsorbed on non-porous adsorbents as a function of P/P_s . The corrections cannot be made without a pore shape model. But, if the second order terms in case of correction for a cylindrical pore model, are neglected, then the corrections become identical for both cylindrical and parallel plate models. The correction terms, in such a case will be

$$V_2 = 10^{-4} (t_1 - t_2) S_1$$
 ...(3a)

$$V_3 = 10^{-4} (t_2 - t_3) (S_1 + S_2)$$
 ...(3b)

Where

 V'_2 , V'_3 are the volume corrections to be applied for the second and third groups of pores, respectively

- S_1 , S_2 are the surface areas of the second, and third groups of pores emptied by capillary evaporation, respectively
- t_1 , t_2 are the thicknesses of the adsorbed films for the first and second groups of pores, in A°.

If volume and surface corrections are employed, the method proposed cannot be regarded as entirely shapeless. Even so, it is a considerable step in that direction. But the corrections add little if any, significant information to that obtainable from uncorrected values. From the above, a cumulative core volume curve can be constructed. This is a plot of V(r) versus r, where V(r) is the volume of all cores that have hydraulic radius 'r' or greater.

The properties of a pore can only be calculated from the core properties with a pore shape model, by the relations

$$\frac{V_{CP}}{V_C} = \left(\frac{2r_C + t}{2r_C}\right)^2 \qquad \dots (4a)$$

$$\frac{S_{CP}}{S_C} = \frac{2r_C + t}{2r_C} \qquad \dots (4b)$$

for cylindrical pores and

$$\frac{V_{PP}}{V_C} = \frac{r_C + t}{r_C} ; S_{PP} = S_C \qquad \dots (5)$$

for parallel plate pores, where the subscripts $_{CP}$ refer to the cylindrical pore, $_{PP}$ to parallel plate pore and $_C$ to the core.

Adsorption and desorption isotherms give different pore structure curve for the same adsorbent by the present method, as by all other methods. But by the method here in described, the desorption isotherm which represents true capillary condensation equilibrium gives reliable results regardless of the shape of the pore (including ink-bottle type of pores) (Brunauer *et al*, 1967b). Whether this view is accepted or not, consistency should be maintained in pore structure analysis, in choosing adsorption or desorption isotherms for comparison purposes.

Materials and Methods

Materials :

In this investigation on alluvial silty soil (LL = 27%, PL = 18%, clay = 18%, silt = 48%, specific surface area = 18.0 m²/g) of the Delhi region was used. The fly ash for this study was collected from Indraprastha Thermal Power Station, Delhi. The grain size distribution of the soil and fly ash used are reported in Figure 1. Reagent grade hydrated



FIGURE 1 Grain size distribution curves

lime was used to minimise compositional variables. The complete investigation was carried on the admixtures as detailed in Table 1, to bring out clearly the effect of addition of lime and fly ash on the pore structure of the silt.

PORE STRUCTURE ANALYSIS

TABLE 1

Admixtures Used

S. No.	Admixtures				
1	Silt				
2	Silt $+ 2\%$ lime				
3	Silt+ 4% lime				
4	Silt 87.5% + Fly ash 12.5%				
5	Silt 75% + Fly ash 25%				
6	(Silt 87.5% + Fly ash 12.5%) + 2% lime				
7	(Silt 87.5% + Fly ash 12.5%) + 4% lime				
8	(Silt 75% + Fly ash 25%) + 2% lime				
9	(Silt 75% + Fly ash 25%) + 4% lime				

Specimen preparation :

The determinations reported herein were carried out on samples compacted statically in a reproducible manner. The admixtures were mixed with water to a consistency amenable for easy compaction. Then samples of 25 mm diameter and 50 mm height of different densities were prepared by static compaction using a specially designed compaction mould (Sridharan, 1968) to get homogeneous samples. To obtain the desorption isotherm, these samples were kept in ten desiccators maintained at relative humidities ranging from 30 to 99 per cent. For every admixture, 7 samples of different void ratios were kept in each desiccator maintained at a particular relative humidity.

Maintenance of constant relative humidity :

Aqueous solutions of sulphuric acid (as per ASTM E 104-51) were used to maintain the different relative humidities. Air tight 250 mm diameter desiccators were used as the containers. The bottom portion contained the sulphuric acid to the required concentration and the samples were kept at the top half over a perforated sheet. The distance between the samples and the solution was kept to a minimum of about 10 mm. The temperature was maintained constant at $22\pm0.5^{\circ}$ C throughout the experiments. Equilibrium was usually obtained in about 6 weeks, but the final weights of all samples were taken only at the end of 8 weeks, and the equilibrium moisture contents determined in grams of water per gram of dry soil. Simultaneously the density of the sulphuric acid solution in each desiccator was determined to know the equilibrium relative humidity. By plotting the equilibrium moisture content against relative humidity, the desorption isotherm is obtained.

Test Results and Discussion

Table 2 gives typical results of the equilibrium desorption moisture contents for various void ratios at different relative pressures for 4 admixtures. In spite of reasonable changes in void ratios, it is seen that the equilibrium moisture contents are little affected, if not same, allowing for experimental errors. Sridharan *et al* (1971) have concluded that for compacted soils, the differential effect of the compaction process is to decrease the content of the gross pores (>4 μ m) and coarse pores (0.14 to 4 μ m)

		Typical equilibrium des	orption water contents		
-		Silt+12.5%	Fly ash		
Sample No.	Void Ratio	<i>W</i> % at $P/P_s = 0.373$	Sample No.	Void Ratio	W% at $P/P_s = 0.852$
	0.857 0.790 0.744 0.697 0.649 0.605 0.545	$1.46 \\ 1.45 \\ 1.48 \\ 1.44 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.46$		0.843 0.789 0.742 0.688 0.640 0.608 0.555	2.98 3.01 3.08 3.09 3.03 3.00 3.00
		(Silt + 12.5%Fly a	sh) + 2% Lime		
Sample No.	Void Ratio	$W\%$ at $P/P_s = 0.373$	Sample No.	Void Ratio	<i>W</i> % at $P/P_s = 0.797$
IV B ₁ IV B ₂ IV B ₃ IV B ₄ IV B ₅ IV B ₆ IV B ₇	0.852 0.828 0.758 0.732 0.651 0.621 0.591	1.18 1.19 1.19 1.16 1.14 1.18 1.19		0.859 0.810 0.776 0.732 0.665 0.610 0.586	2.97 2.90 2.87 2.86 2.84 2.97 2.89
		(Silt + 25% Fly a	ish) + 4% Lime		
Sample No.	Void Ratio	$W\%$ at $P/P_s = 0.986$	Sample No.	Void Ratio	$W\%$ at $P/P_s = 0.840$
$\begin{array}{c} \mathrm{IX} \ \ \mathrm{J_1} \\ \mathrm{IX} \ \ \mathrm{J_2} \\ \mathrm{IX} \ \ \mathrm{J_3} \\ \mathrm{IX} \ \ \mathrm{J_4} \\ \mathrm{IX} \ \ \mathrm{J_5} \\ \mathrm{IX} \ \ \mathrm{J_6} \\ \mathrm{IX} \ \ \mathrm{J_7} \end{array}$	0.916 0.854 0.794 0.720 0.689 0.670 0.660	7.88 7.92 7.82 7.97 7.96 7.84 7.88	IX F_1 IX F_2 IX F_3 IX F_4 IX F_5 IX F_6 IX F_7	0.980 0.862 0.771 0.759 0.756 0.702 0.635	3.22 3.20 3.20 3.12 3.19 3.11 3.20

only and that fine and very fine pore size ranges (<0.14 μ m) are virtually unaffected. It can be easily shown that in practice to attain equilibrium under high relative humidities (99 per cent and above) it takes infinitely long time. Since larger pores attain equilibrium under higher relative humidities (for e.g. at 99% relative humidity, pores having a diameter of 0.2 μ m will be filled), it requires infinitely long time to reach equilibrium and hence results obtained at very large relative humidities are expected to be insensitive with regard to change in void ratios. This trend has been observed by Sridharan and Venkatappa Rao (1975 *a*, *b*) for various soils. Thus, the results (Table 1) obtained presently for various lime fly ash admixtures exhibit the same trend as observed earlier, viz. compaction process brings about changes in gross and coarse pores, rather than fine to very fine pores.

Figures 2 to 5 show the desorption isotherms obtained for the various admixtures. Since, the change in void ratio did not effect the equilibrium moisture content, the desorption isotherm shown for a particular soil is same irrespective of the differences in void ratio. This clearly shows that the procedure described here (or any other method which uses the sorption isotherms for analysis of pore structure) could be applied only for the measurement of fine pore size ranges.

A study of the sorption isotherms (Figures 2 to 5) shows that the isotherms are relatively flat upto a relative humidity of 50-60 per cent, later the slope gradually increases and beyond about 90 per cent they are very steep.

Table 3 gives the analysis of the desorption isotherm for compacted silt. The first two columns give the actual isotherm data per gram of adsorbent (soil). Column-3 gives the volume desorbed in ml/g of adsorbent when the relative pressure (P/P_s) is lowered to the value given in column-1 from the value in the row above. This is the uncorrected





TABLE	3	
	-	

Pore dia. (µm)	
0.4228	INDÍA
0.12192	z
).05768	Ġeot
0.03960	ECI
0.02504	INIC/
0.01756	F
.01256	JÓUR
.00976	NAL

Analysis of Water Vapour Desorption Isotherm of Silt

P/P_s	Eq. M.C. (CC water per g. of soil)	V _{desorbed} (uncorr) (ml)	V _{desorbed} (corr) (ml)	S(_{uncorr}) (m²/g)	S(corr) (m²/g)	r_h (core) (uncorr) (A°)	r_{h} (core) (corr) (A°)	r_{h} (Pore) (A°)	Pore dia. (µm)
1.0	0.0960		0.0.0.0.0000000	a and a second					
0.99	0.08445	0.01195	0.01195	0.11398	0.11398	1048.42	1048.40	1057.0	0.4228
0.975	0.0625	0.02195	0.02192	0.73662	0.73561	297.90	297.98	304.8	0.12192
0.95	0.0510	0.0115	0.01137	0.83274	0.82332	138.10	138.10	144.2	0.05768
0.925	0.0432	0.0078	0.00762	0.95652	0.93440	81.54	81.54	84.9	0.03960
0.90	0.0396	0.0036	0.0034	0.62643	0.59170	57.50	57.46	62.6	0.02504
0.85	0.0351	0.0045	0.0041	1.11178	1.04026	39.50	39.41	43.9	0.01756
0.80	0.0318	0.0033	0.0029	1.20636	1.06013	27.40	27.35	31.4	0.01256
0.75	0.0290	0.0028	0.0024	1.35619	1.16244	20.64	20.64	24.4	0.00976
0.70	0.0265	0.0025	0.0021	1.52767	1.28324	16.36	16.36	19.8	0.00792
0.65	0.0236	0.0029	0.0024	2.16595	1.79250	13.40	13.38	16.5	0.00660
0.60	0.0219	0.0017	0.0011	1.51828	0.98241	11.20	11.19	14.1	0.00564
0.55	0.0200	0.0019	0.0015	1.99790	1.57728	9.50	9.50	12.24	0.00489
0.50	0.0185	0.0015	0.00095	1.83645	1.16308	8.10	8.10	10.92	0.00437



FIGURE 3 Water vapour desorption isotherms for silt with fly ash



FIGURE 4 Water vapour desorption isotherms for silt+12.5% fly ash with lime

volume. The surface area (uncorrected) is obtained by using Kieslev's equation, taking $\gamma = 71.97$ dynes/cm and $R = 8.315 \times 10^7$ erg/deg mole in Equation 2 and given in column 5. This is the (uncorrected) surface area of the cores that form upon emptying of the pores, when water desorbs by the amount given in column 3. Having determined the surface area and volume (uncorrected) the uncorrected hydraulic radius can be obtained as per equation-1, and is tabulated in column 7.



FIGURE 5 Water vapour desorption isotherms for silt+25% fly ash with lime

Corrections for the values obtained above can be done only with the help of a t-curve. The t-curve to be used for the analysis of a given adsorbent is the one which has the same heat of adsorption (or the same 'C' constant of a BET plot) as the adsorbent and in the water vapour adsorption the nature of the surface plays an important role. In the present analysis, t-curve presented by Hagymassy et al (1969) is made use of. Knowing the uncorrected surface area and the *t*-curve for water, the corrections for volume desorbed are applied using the relationships given in Equation 3 and the corrected volumes are tabulated in column 4. The corrected surface areas of the cores are again calculated using Kiesley's equation and recorded in column 6. By dividing column 4 by column 6 the corrected hydraulic radius of the cores is obtained and is given in column 8. It is easily seen that the values of the hydraulic radii of the cores-uncorrected (column 7) and corrected (column 8) are very close to each other.

From the above structure analysis, using the relationships for a cylindrical pore model (Equation 4a) and the *t*-curve for water, the pore properties are obtained and the hydraulic radii of the pores recorded in column 9. From columns 7, 8 and 9 of Table 3 it may be observed that there is practically no significant difference in the values of the hydraulic radii obtained by the different procedures. Similar conclusion was arrived earlier by Brunauer et al (1967a) for hardened Portland cement pastes and Sridharan and Venkatappa Rao (1975 a, b) for different soils. Though not presented here to conserve space, the behaviour is similar for the various soil lime and fly ash admixtures studied.

The pore diameter, calculated from the hydraulic radius (column 9) using a cylindrical pore model, is reported in column 10. Using similar

PORE STRUCTURE ANALYSIS

data obtained for various admixtures, the pore size distributions are presented in Figures 6 to 9. In these figures, the volume desorbed is plotted as a cumulative curve, the volume decreasing from the largest pores on the right, to the smallest on the left. The total pore volume is indicated by the horizontal bars on the ordinate, thus making obvious the extent to which pores have not been described by this procedure. For observing more clearly the differences in pore size distribution, the pore spectra are presented as bar charts in Figures 10 and 11.

From Figure 10, it may be seen that there is a decrease in percentage pore volume of pores larger than 0.1 μ m dia., when lime is added. The decrease is considerable for pores > 0.4 μ m, and 0.2-0.4 μ m and marginal for pores 0.1-0.2 μ m. On the other hand the pore volume for pores of 0.1-0.004 μ m range increases on addition of lime. This increase is quite significant for pores of 0.04-0.1, 0.02-0.04, 0.02-0.01 μ m size ranges and marginal for pores of 0.004-0.01 μ m. For pores of size 0.002-0.004 μ m, there is once again a decrease in pore volume and the pore



FIGURE 6 Pore size distribution curves for silt with lime



FIGURE 7 Pore size distribution curves for silt with fly ash



FIGURE 8 Pore size distribution curves for silt+12.5% fly ash with lime



FIGURE 9 Pore size distribution curves for silt+25% fly ash with lime

volume for pores smaller than 0.002 μ m decreases nearly by half. Thus, the effect of addition of lime to silt is to decrease the number of pores larger than 0.1 μ m and smaller than 0.004 μ m and to increase the number of pores of 0.004-0.1 μ m range. Further, it has already been stated earlier that the pores larger than 0.4 μ m are not characterized by this method. As there is a clear decrease in the volume of pores of this range on addition of lime, which shows that all the pores in lime treated silt are measurable by the method used. From Figure 6, it may also be seen that the d_{50} of the silt decreases from 0.047 μ m to 0.031 μ m on addition of 2 per cent lime and to 0.029 μ m on addition of 4 per cent lime. Thus the effect of addition of lime is essentially to decrease the pore size.

The addition of fly ash (Figure 10) causes an increase in pore volume of pores larger than 0.4 μ m and considerable decrease of pore volume for pores of 0.2-0.4 μ m and all other smaller size ranges upto 0.002 μ m, except in case of 0.1-0.04 μ m where an increase is observed. The pore





à,



FIGURE 11 Bar diagram of percent pore volume versus pore diameter for silt with lime and fly ash

volume for pores smaller than $0.002 \ \mu m$ remains unchanged. Thus it may be generally concluded that the effect addition of fly ash is to increase the number of pores for sizes, larger than $0.4 \ \mu m$ and $0.04 - 0.1 \ \mu m$, and to decrease the number of pores of all other sizes, excepting those smaller than $0.002 \ \mu m$ for which the number remains nearly constant. Further, from Figure 7, it can be seen that d_{50} of the silt increases from $0.047 \ \mu m$ to $0.053 \ \mu m$ when 12.5 per cent fly ash has been added and to $0.062 \ \mu m$ when 25 per cent fly ash has been added. Thus the effect of addition of fly ash is essentially to increase the presence of larger pores.

On comparison of lime-fly ash treated silt with untreated silt, (Figure 11), it is seen that for pore sizes 0.2-0.4, 0.1-0.2, 0.01-0.004, 0.002- $0.004 \ \mu m$ and smaller than $0.002 \ \mu m$, there has been a decrease in pore volume which can be clearly attributed to the cumulative effects of lime and fly ash (in both cases a decrease in pore volume was noted earlier, for these size ranges). On the other hand for pore size ranges > 0.4 μ m, 0.04-0.1, 0.02-0.04 and $0.01-0.02 \ \mu m$ there is a significant increase in pore volume which again is primarily a result of the cumulative effect of lime and fly ash. These changes have been similar for all the lime fly ash silt mixtures. From Figure 8, it may be seen that value of d_{50} for silt treated with 12.5 per cent fly ash is 0.042 μ m when 2 per cent lime is added and 0.037 μ m when 4 per cent lime is added. The value of d_{50} for silt treated with 25 per cent fly ash is 0.044 μ m for 2 per cent lime and 0.042 μ m for 4 per cent lime. The decrease observed in all the mixes used (compared with 0.047 μ m for untreated silt) shows that the decrease is primarily influenced by lime which over rides the effect of fly ash. But because of this effect of fly ash, the decrease in d_{50} is not as significant as in lime alone and all the values observed are higher than d_{50} values for addition of lime alone and this decrease is much less for 25 per cent fly ash as compared to 12.5 per cent fly ash.

The above analysis of pore structure has been extensively used by the authors for analysis of negative pore water pressure and the understanding of the strength behaviour of partly saturated stabilized soils. The details will appear separately.

Conclusions

Pore size distributions of a compacted alluvial silt with lime upto 4 per cent) and fly ash (upto 25 per cent) as additives have been obtained by analysing water vapour desorption isotherms by Brunauer's modelless method. The following conclusions are drawn:

- 1. The method used successfully brings out changes in pore sizes ranging from 0.4-0.002 µm of silt treated with additives.
- 2. The effect of addition of lime to silt is to decrease the number of pores larger than 0.1 μ m and smaller than 0.004 μ m and to increase the number of pores larger than 0.004-0.1 μ m.
- 3. On addition of fly ash, the number of pores increases for sizes larger than 0.4 μ m and 0.04-0.1 μ m and decreases the number of pores of all other sizes.
- 4. The effect of addition of lime and fly ash is to increase significantly the pores of sizes > $0.4 \ \mu m$, 0.04-0.1, 0.02-0.04 and $0.01-0.02 \ \mu m$ and to decrease the number of pores for other sizes ranges.
- 5. The d_{50} value of silt decreases significantly on addition of lime and increases significantly on addition of fly ash. When both lime and fly ash are added the d_{50} value increases when compared to untreated silt, but not as much as when treated with fly ash alone.

References

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BROEKHOFF. J.C.P. and LINSEN, B.G. (1970): "Pore Systems in Adsorbents and Catalysis", *Physical and Chemical Aspects of Adsorbents and Catalysts*, Linsen, B.G. (Ed) Academic Press, New York.

BRUNAUER, S. EMMETT, P.H. and TELLER, E. (1938): "Adsorption of Gases in Multimolecular Layers", J. of American Chemical Society, 60, pp. 309-319.

BRUNAUER, S., MIKHAIL, R.S.H., and BODOR, E.E. (1967a): "Pore Structure Analysis without a Pore Shape Model", J. of Colloid and Interface Science, 24, pp. 451-463.

BRUNAUER, S., MIKHAIL, R.S.H. and BODOR, E.E. (1967b): "Some Remarks about capillary condensation and Pore Structure Analysis", J. Colloid and Interface Science, 25, pp. 353-358.

CHILDS, E.C. and COLLIS-GEORGE, N. (1950): "The Permeability of Porous Materials", Roy. Soc. (London) Proc. A, Vol. 201, pp. 392-405.

CRANSTON, R.W. and INKLEY, E.A. (1957): "The Determination of Pore Structures from Nitrogen Adsorption Isotherms", *Advances in Catalysis*, Academic Press, New York, Vol. 9, pp. 143-154.

ESMER, E., WALKER, R.D. and KREBS, R.D. (1969): "Freeze-Thaw Durability of Lime-Stabilized Clay Soils", *Highway Research Record*, No. 263, pp. 27-36.

HAGYMASSY, J., BRUNAUER, S. and MIKHAIL, R.S.H., (1969): "Pore Structure Analysis by Water Vapour Adsorption, 1-t—curves for Water Vapour", Journal of Colloid and Interface Science, Vol. 29, pp. 483-491.

HUANG, R.J. and DEMIREL, T. (1973): "Micropore size Analysis of a friable Loess", *Highway Research Record*, 429, pp. 1-13.

KLOCK, G.O., BOERMA, L. and DEBACKER, L.W. (1969): "Pore Size Distributions as measured by the mercury intusion method and their use in predicting permeability", *Proc. Soil Science Soc. America*, Vol. 33, No. 1, pp. 12-15.

MARSHALL, T.J. (1958): "A relation between Permeability and Size Distribution of Pores", Journal of Soil Science, Vol. 9, pp. 1-8.

MILLINGTON, R.J. and QUIRK, J.P. (1959): "Permeability of Porous media", *Nature*, 183, pp. 387-388.

OLSEN, H.W. (1962): "Hydraulic Flow Through Saturated Clays", Clays and Clay minerals, Vol. 11, Pergamon New York, pp. 131-161.

RITTER, H.L. and DRAKE, L.L. (1945): "Pore-size distribution in Porous Materials: Pressure Porosimeter and Determination of complete Macroporesize Distribution" Industrial & Engg. Chemistry Anal. Ed. Vol. 17, pp. 782-786.

ROBERTS, B.F. (1967): "A Procedure for Estimating Pore Volume and Area distribution from Sorption Isothe ms", *Journal of Colloid and Interface Science*, Vol. 23, No. 2, pp. 266-277.

SRIDHARAN, A. (1968) : "Some Studies on the Strength of partly Saturated clays", *Ph. D. Thesis*, Purdue University, Lafayette, Indiana.

SRIDHARAN, A., ALTSCHEFEL, A.G. and DIAMOND, S. (1971): "Pore size Distribution studies", Journal of Soil Mech. and Found. Divn., Proc. ASCE, Vol. 97, (SM5), pp, 771-787.

SRIDHARAN., A. and VENKATAPPA RAO, G. (1975a): "Pore size distributions in compacted Soils", *Proc. Istanbul Conf. on Soil Mechanics and Found. Engg.*, Turkey, Vol. 1, pp. 75-84.

SRIDHARAN, A. and VENKATAPPA RAO, G. (1975b): "Pore size Distributions in compacted Soils", Proc. First Baltic Conf. on Soil Mechanics and Found. Engg., Poland, pp. 365-372.

VENKATAPPA RAO, G. (1972) : "Physico-chemical Mechanisms Controlling Volume change and Shear Behaviour of Clays", *Ph.D. Thesis*, Indian Institute of Science, Bangalore.

VENKATAPPA RAO, G. and SRIDHARAN, A. (1978): "Strength Behaviour of partially saturated clays", *Proc. Conf. on Geotechnical Engineering*, New Delhi, Vol. I, pp. 124-129.