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Specific Surface Area and Pore Size Distribution: How these parameters affect engineering behavior of fine grained soils

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Specific Surface Area

The engineering characteristics of fine-grained soils

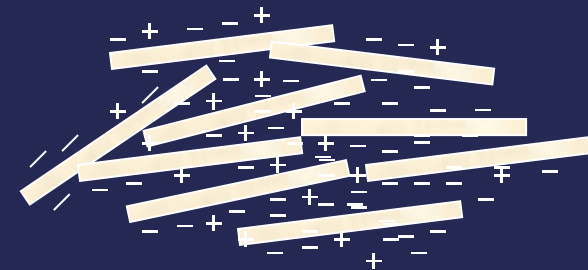
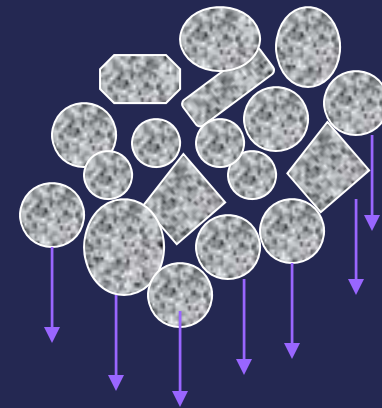


greatly influenced

Physico-chemical interactions present in the clay-water electrolyte system.

Specific Surface Area

- Coarse-grained soils:
 - Self-weight forces
 - Skeletal forces
- Fine-grained soils:
 - Electrical forces
 - Capillary forces



Specific Surface Area

Definition of Specific Surface Area?

The specific surface area (SSA)



the ratio of its surface area A_s to its mass M

$$SSA = A_s / M \implies \text{m}^2\text{g}^{-1}.$$

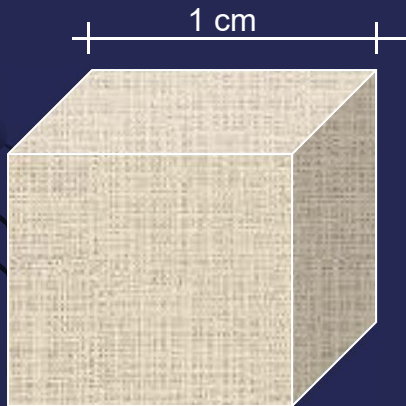
Specific Surface Area

Inverse relationship between the grain size and surface area

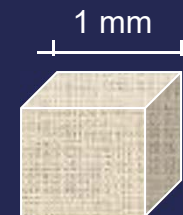
Grain size



Surface area

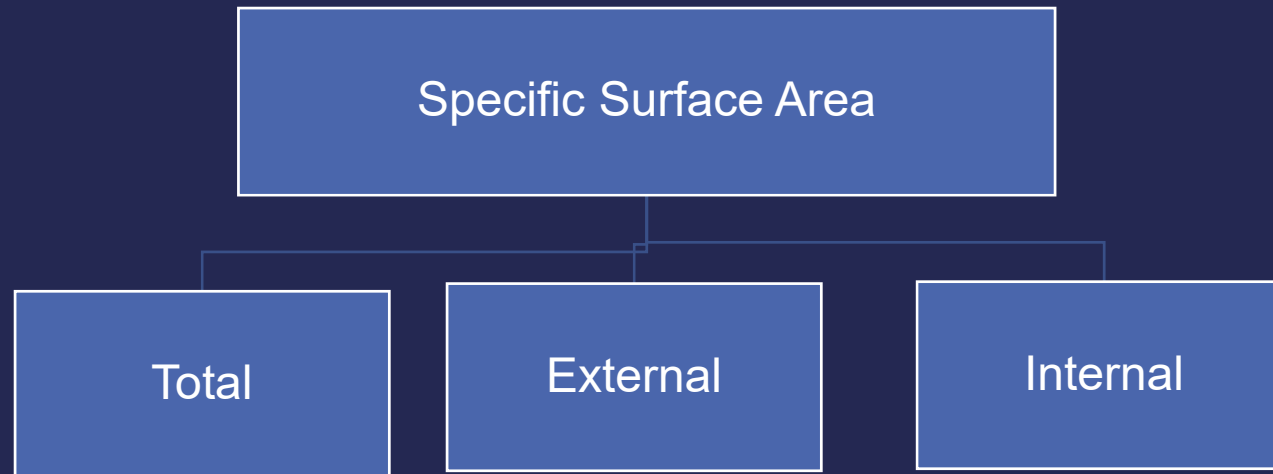


$$SSA = \frac{6(1\text{cm}^2)}{1\text{cm}^3} = 6 / \text{cm} = 0.6 / \text{mm}$$



$$SSA = \frac{6(1\text{mm}^2)}{1\text{mm}^3} = 6 / \text{mm}$$

Specific Surface Area

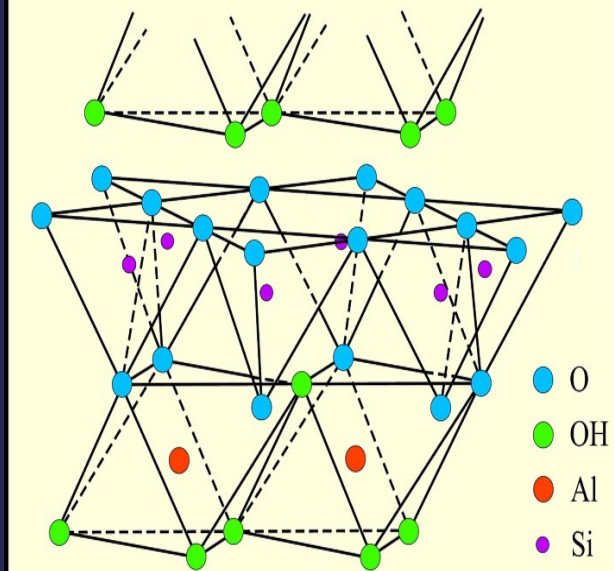


Bonds between the layers of the clay minerals (after Mitchell, 1993)

Clay mineral	Chemical designation	Bonds between layers
Kaolinite	$\text{Al}_4 \text{Si}_4 \text{O}_{10}(\text{OH})_8$	O-OH, strong
Illite	$(\text{K}, \text{H}_2\text{O})_2 \text{Si}_8(\text{Al}, \text{Mg}, \text{Fe})_{4,6} \text{O}_{20}(\text{OH})_4$	K-ions, strong
Montmorillonite (Smectite group)	$\text{Si}_8(\text{Al}_{3.34} \text{Mg}_{0.66}) \text{O}_{20}(\text{OH})_4$	O-O, very weak, swellable
Chlorite	$(\text{SiAl})_8(\text{Mg}, \text{Fe})_6 \text{O}_{20}(\text{OH})_4$ (2:1 layer)	$(\text{MgAl})_6(\text{OH})_{12}$

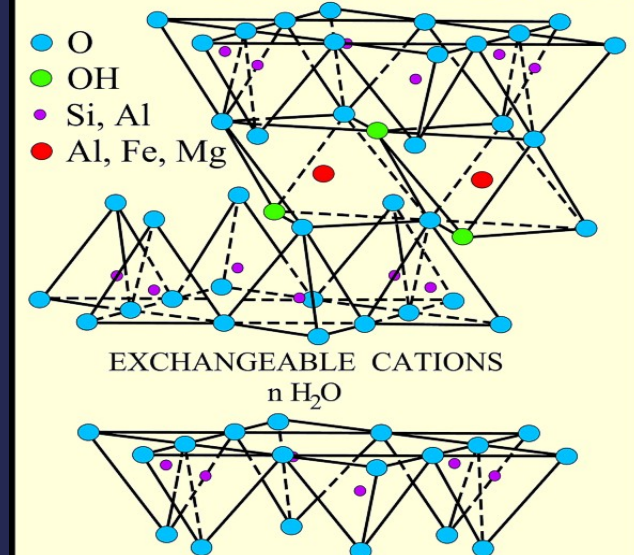
Specific Surface Area

STRUCTURE OF A KAOLINITE LAYER

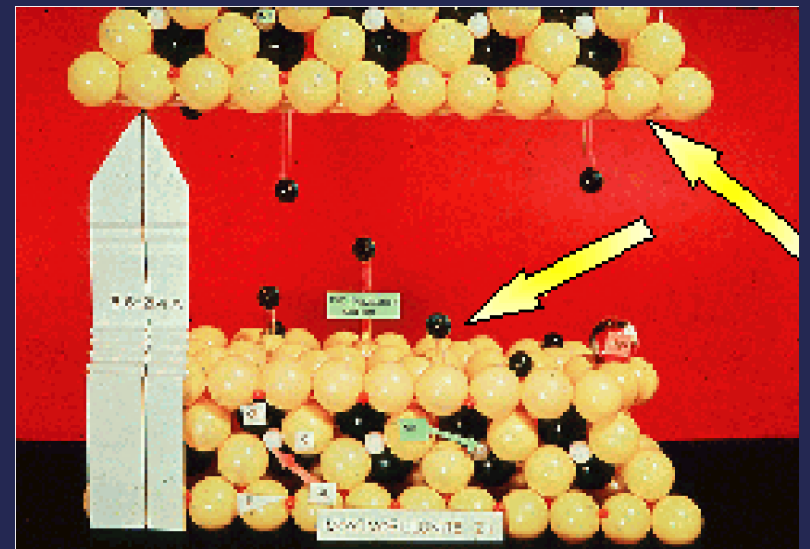
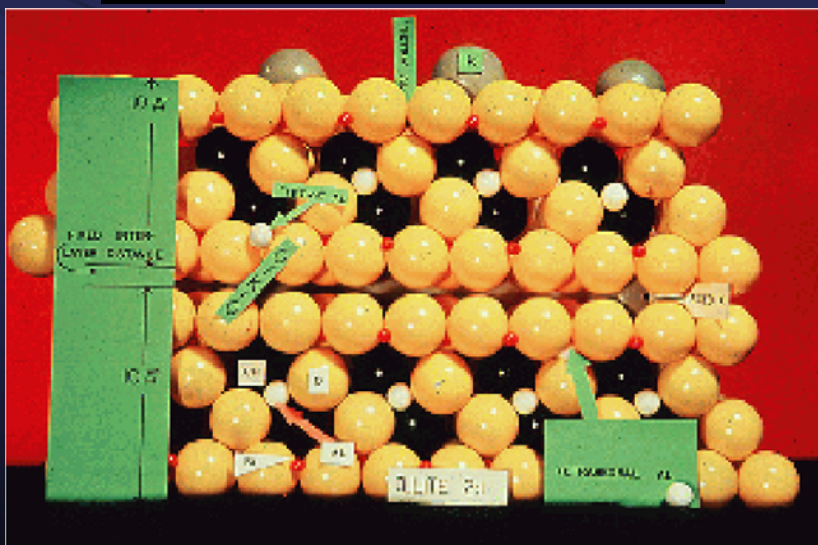


MODIFIED FROM GRIM (1962)

STRUCTURE OF MONTMORILLONITE



MODIFIED FROM GRIM (1962)



Specific Surface Area

SSA constant property. It does not change with water content or time.

SSA varies with mineralogy !!!!!

Specific surface area of common clay mineral constituents of fine-grained soils (after Mitchell, 1993)

Clay Mineral	Structure	External SSA (m ² g ⁻¹)	Internal SSA (m ² g ⁻¹)
Halloysite	1:1	10-20	-
Kaolinite	1:1	35-70	-
Smectite	2:1	50-120	700-850
Illite	2:1	65-100	-
Vermiculite	2:1	40-80	800-900
Chlorite	2:1:1	10-40	-

Specific Surface Area

The importance of surface area can be inferred by comparing the magnitude of interparticle forces F_{elec} to the weight W of a particle (Santamarina et al., 2002):

$$\frac{F_{elec}}{W} = \frac{A_s \times (R_{ddl} - A_{tt})}{Mg} = SSA \frac{(R_{ddl} - A_{tt})}{g}$$

g is acceleration (in m/s^2),

R_{ddl} and A_{tt} are the repulsion and attraction electrical forces acting between two particles (in N/m^2).

Specific Surface Area

SSA determination methods:

- Gas adsorption:
 - Nitrogen (N₂) adsorption
 - Water vapor adsorption
- Polar liquid adsorption:
 - Ethylene glycol monoethyl ether (EGME)
 - Methylene Blue (titration or spot test methods)

Other polar liquids: ethylene glycol (EG), cethyl pryidinium bromide (CPB), p-Nitrophenol (pNP), polyvinylalcohol (PVA), ethylene oxide chain, etc.

Specific Surface Area

Definition of SSA  straightforward

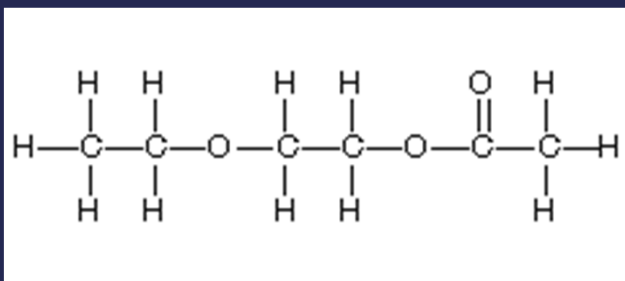
Accurate measurement  difficult

Measurement methods yield widely different results.

Specific Surface Area

Ethylene Glycol Monoethyl Ether (EGME) Adsorption Method

➡ Wetting a sample with excess ethylene glycol.



Ethylene glycol monoethyl ether (EGME) structure

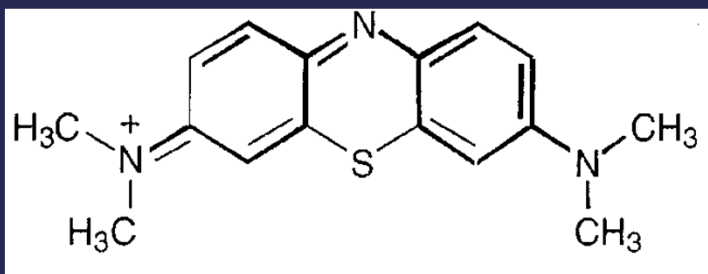
➡ Equilibrating and removing excess liquid by the evacuation.

➡ The mass of the retained liquid under the assumption that a monomolecular layer of ethylene glycol was adsorbed on the surface.

Specific Surface Area

Methylene Blue (MB) Adsorption Method

➡ Wetting a sample with methylene blue.



Methylene Blue Cation

Dimensions of 17 Å × 7.6 Å × 3.25 Å



Light blue halo

Specific Surface Area

BET- N₂ dsorption Method



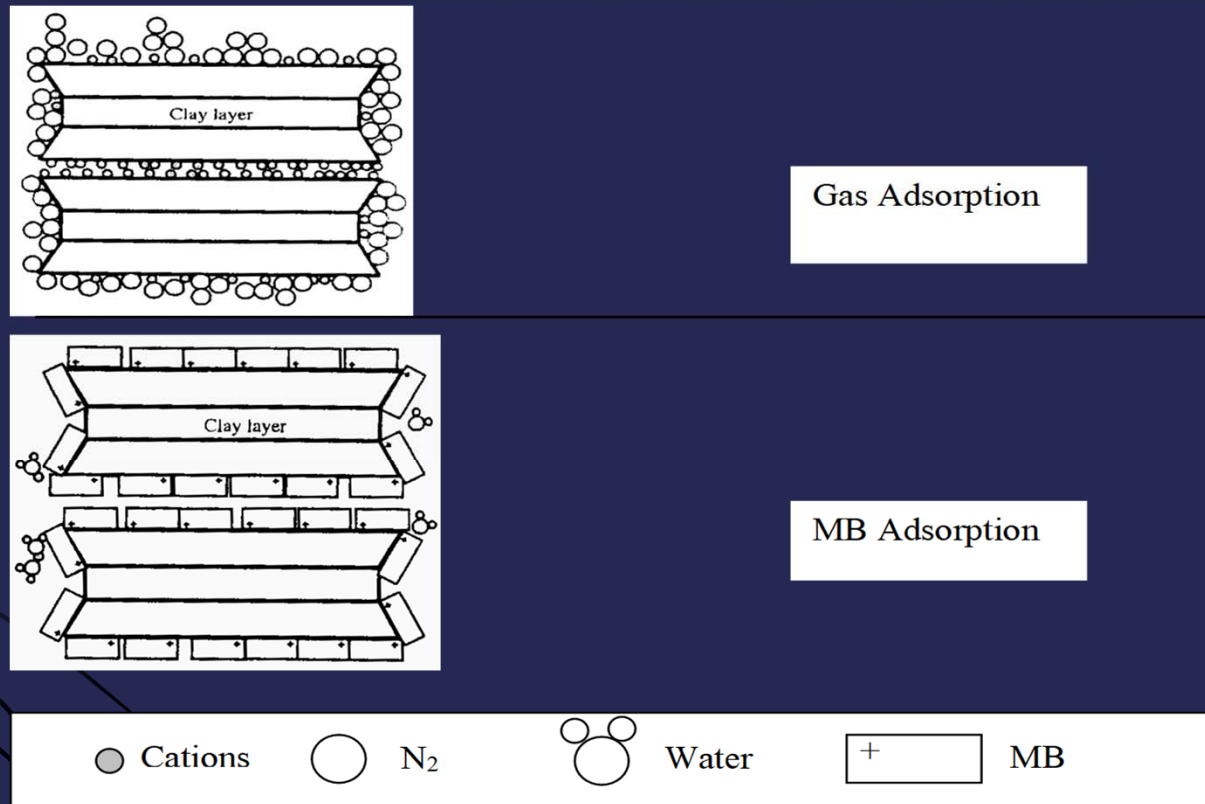
The adsorption of nitrogen and the application to the isotherms of the BET (Brunauer, Emmett, Teller) equation



Quantochrome Monosorb® apparatus for BET-N₂ analysis

Specific Surface Area

Gas Adsorption and Polar Liquid Adsorption Methods



Schematic representation of gas adsorption (dry) and MB (wet) techniques (adapted from Santamarina et al., 2002).

Specific Surface Area

Specific surface area has determining influence on macro engineering properties such as (Smith et al., 1985; Muhunthan, 1991; Jong, 1999):

- Soil index properties (consistency limits, cation exchange capacity, etc.)
- Compressibility
- Permeability
- Shrink-swell potential
- Shear strength
- Electrical conductivity
- Soil stabilization

Specific Surface Area

Specific Surface Area and Liquid Limit (w_L)

Correlation Equation	Correlation Coefficient (r)	Range/Method - Soil Origin	Reference
$w_L = 0.21 \text{ SSA} + 19$	-	South African Soils	De Bruyn et al. (1957)
$\text{SSA} = 1.48 w_L - 14$	0.91	Water adsorption - British Clayey Soils	Farrar & Coleman (1967)
$w_L = 0.56 \text{ SSA} + 19$	0.91	Water adsorption - British Clayey Soils	Farrar & Coleman (1967)
$\text{SSA} = 9.258 \times 10^{-3} w_L^{2.084}$	0.93	BET-N ₂ method - South African / Georgia / Missouri Clayey Soils	Hammel et al. (1983)
$w_L = 0.141 \text{ SSA} + 19.805$	0.82	EGME method - Israel Clayey Soils	Smith et al. (1985)
$w_L = 1.01 \text{ SSA} + 46.5$	-	$w_L > 50$ – BET-N ₂ method -Marine Sediments (Africa / Sulu Sea/ Gulf of Mexico)	Wetzel (1990)
$w_L = 0.82 \text{ SSA} + 40.3$	0.77	BET-N ₂ method - New Zealand and Fijian Soils	Churchman &Burke (1991)
$w_L = 1.2 \text{ EGME Retained} + 26$	0.91	EGME method – New Zealand and Fijian Soils	Churchman &Burke (1991)

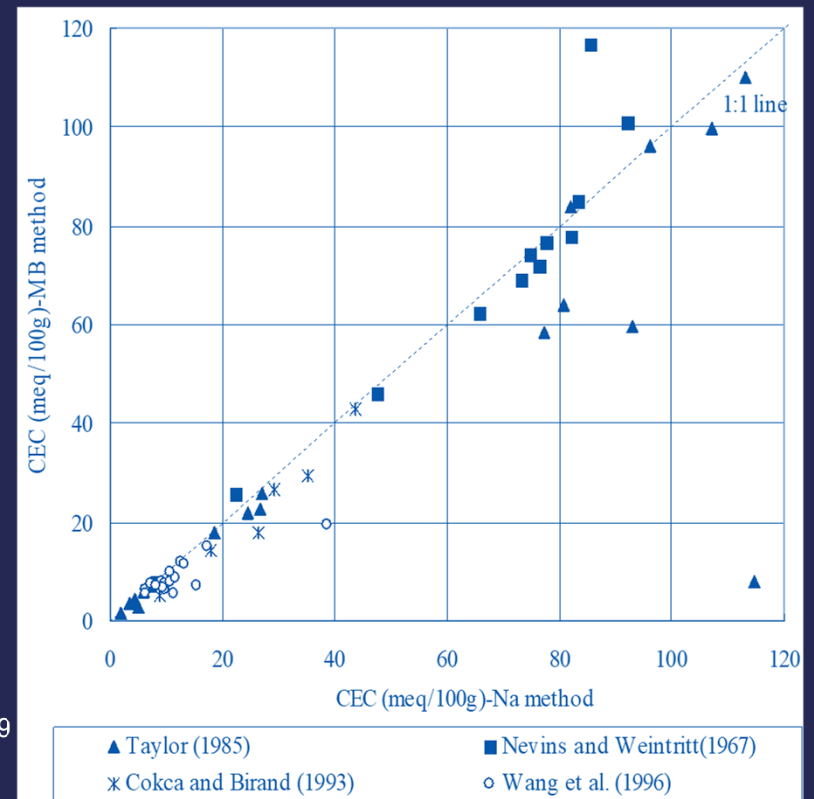
Specific Surface Area

Specific Surface Area and Cation Exchange Capacity (CEC)

Correlations between the specific surface area and cation exchange capacity

Correlation Equation	Range- Soil Origin	Reference
$CEC = 2 + 0.28 \text{ SSA}$	British Clayey Soils	Farrar & Coleman (1967)
$CEC = 2.14 + 0.354 \text{ MB ads.}$	Northwestern Alberta	Soon (1988)
$CEC = 0.54 \text{ EGME retention} - 6.1$	New Zealand and Fijian Soils	Churchman & Burke (1991)
$CEC = 0.14 \text{ SSA} + 3.6$	Osaka Bay clay	Tanaka & Locat (1999)

CEC-Na and CEC-MB comparison



Specific Surface Area

Specific Surface Area and Permeability (k)

- Kozeny-Carman equation for generalized seepage velocity for porous media

$$k = (\gamma / \mu)(1 / C_{K-C})(1 / S_0^2)[e^3 / (1 + e)]$$

μ = viscosity of permeant

C = Kozeny-Carman empirical coefficient

S_0 = specific surface area per unit volume of particles (1/cm)

e = void ratio

γ = unit weight of permeant

Pore Size Distribution

Importance of pore size distribution !

Soils can show different behavior, even at same void ratio!



The reason is difference in the arrangement of soil particles

Soil, consisting of large pores may behave in different ways from that consisting small pores.

Large pores	→	hydraulic conductivity is high
Small pores	→	hydraulic conductivity is low



Pore Size Distribution

Pore size distribution  quantitatively Mercury Intrusion Porosimetry (MIP)

 MIP requires dehydrated samples

The samples can be dehydrated by several methods;

- Air-Drying
- Oven-Drying
- Freeze-Drying
- Critical Point Drying

Shrinkage process occur during the air and oven drying.

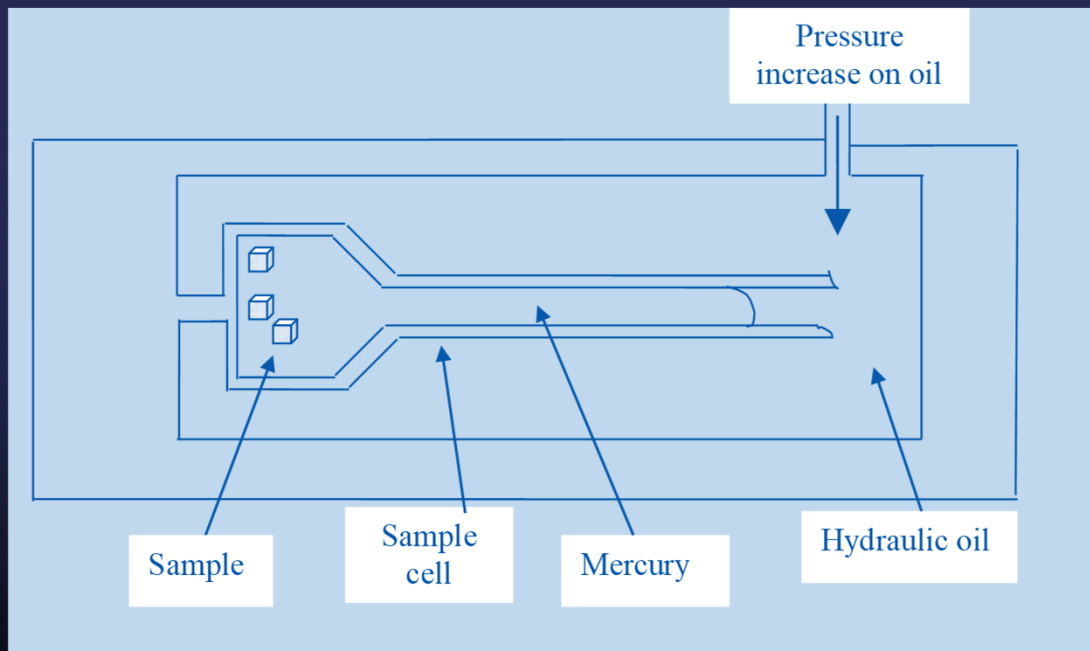
Pore Size Distribution

Mercury Intrusion Porosimetry (MIP)

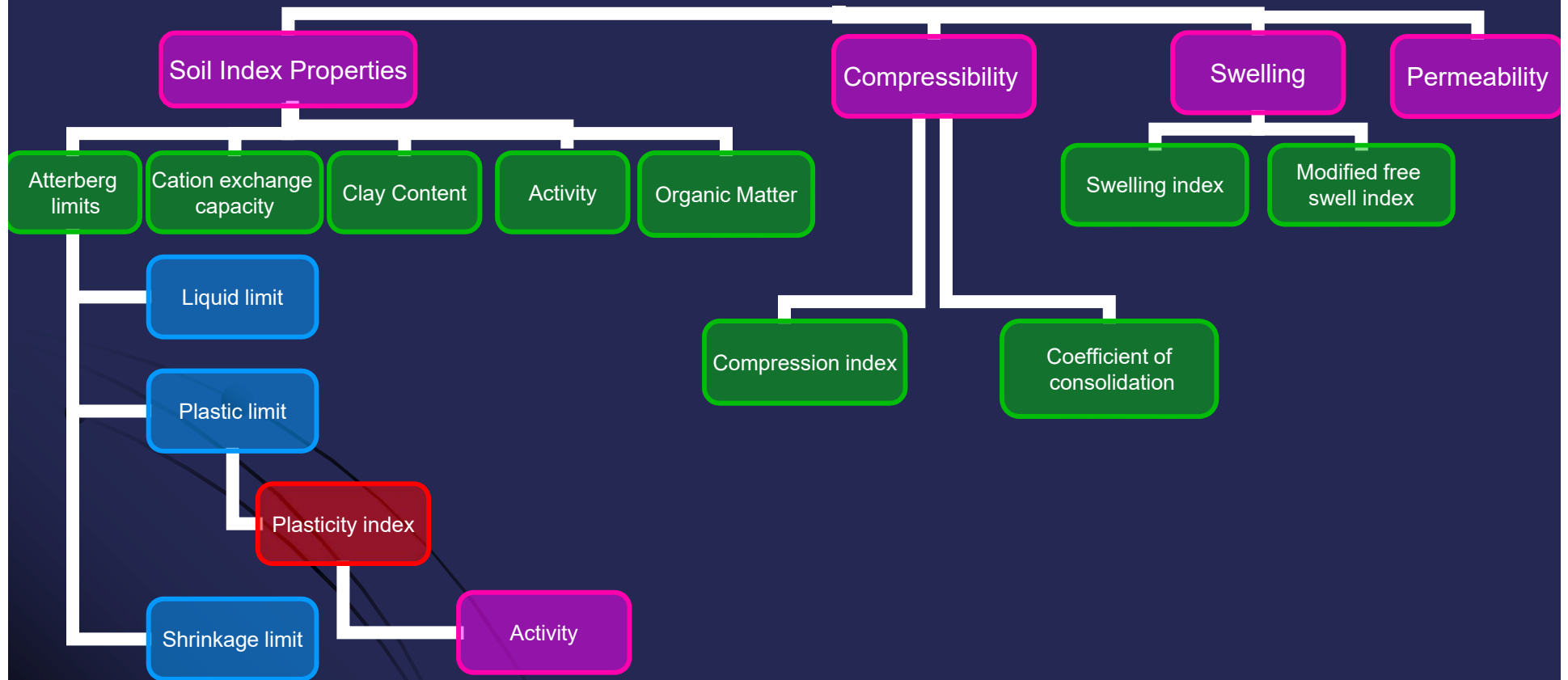
$$D = -\frac{4\gamma \cos \theta}{P}$$

D = pore diameter
 γ = surface tension of mercury
 θ = contact angle between mercury and the pore wall
P = applied pressure.

Washburn (1921) equation



SSA Related Properties:



Specific surface area tests

BET-N₂

MB-spot

MB-titration

EGME



Pore size determination test steps!

Sample preparation



Drying



Pore size determination



Freeze-dryer



Mercury Intrusion Porosimeter

Comparison of SSA determination methods

BET-N₂ SSA values are lower than MB and EGME methods.

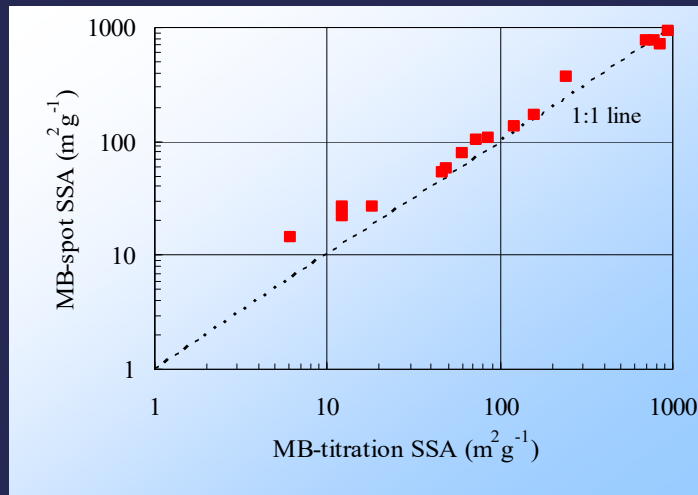
N₂ molecule non-polar → cannot penetrate into internal layers!!!



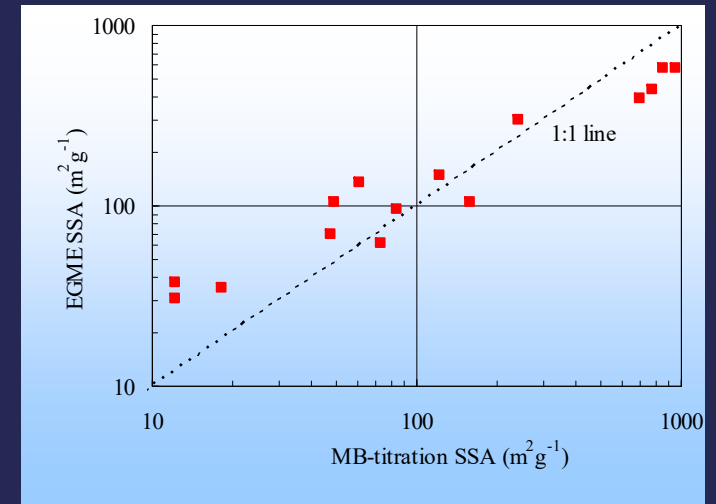
Comparison of SSA determination methods

Selected results from SSA determination methods comparisons:

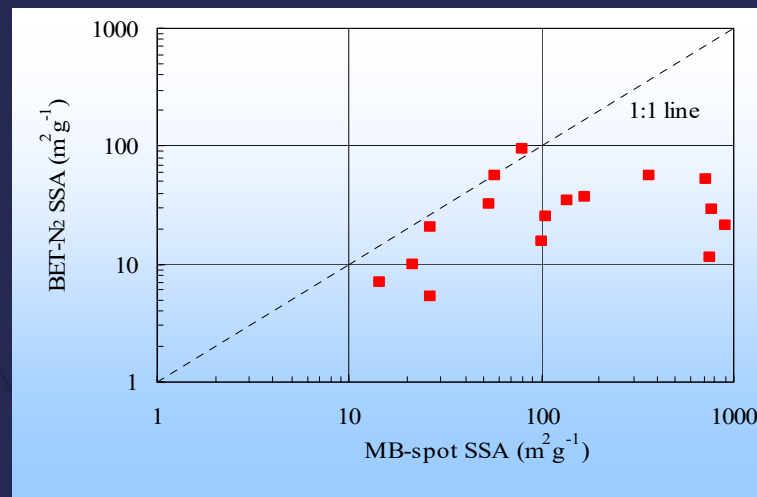
MB-titration vs. MB-spot ($r = 0.99$)



MB-titration vs. EGME ($r = 0.97$)



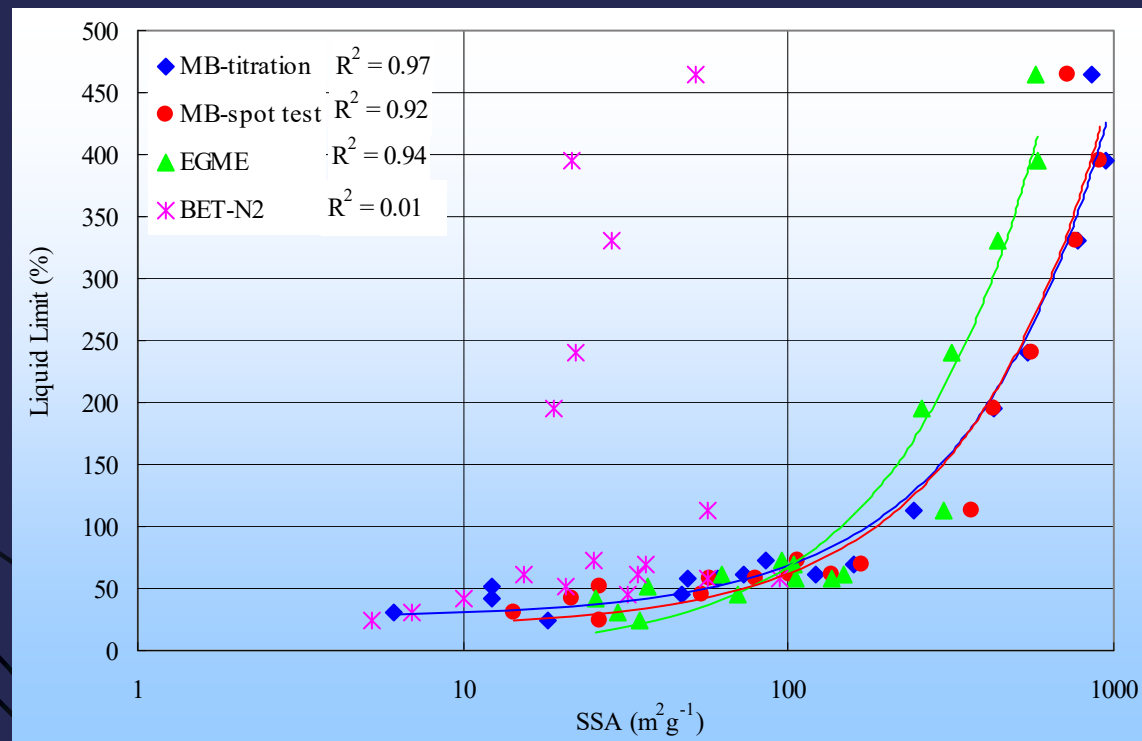
MB-spot vs. BET- N_2 ($r = 0.17$)



SSA and Atterberg limits relationship

SSA versus Liquid Limit

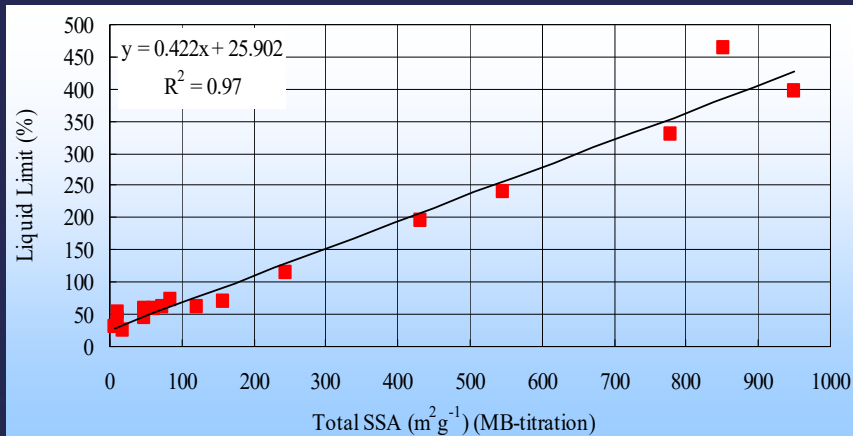
There is an almost linear relationship between the SSA and liquid limit.



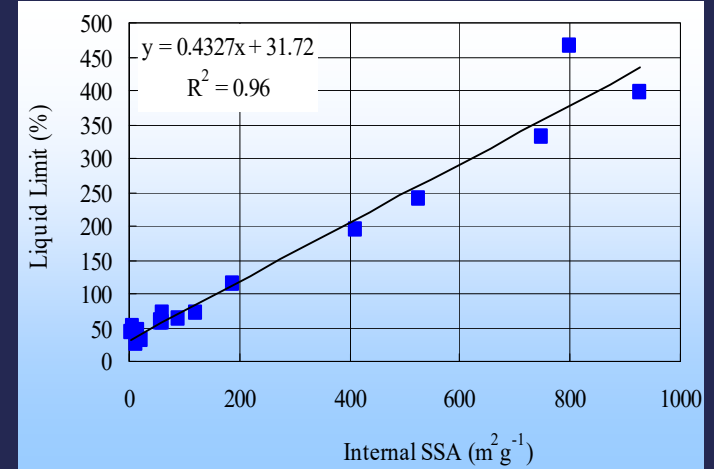
SSA and Atterberg limits relationship

Internal SSA has determining effect on liquid limit!

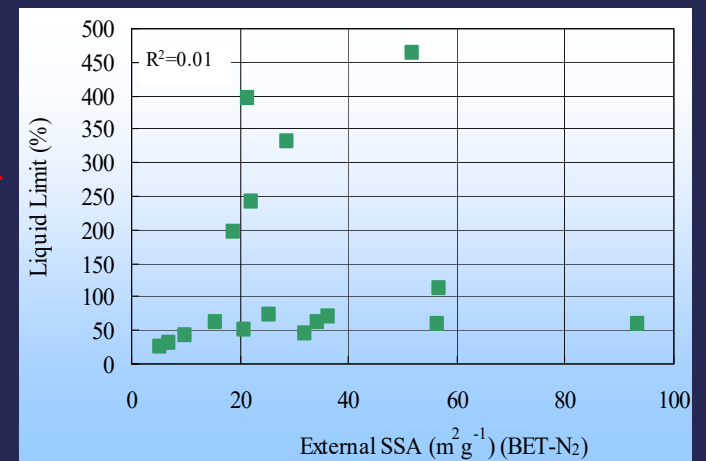
Total SSA versus Liquid limit



Internal SSA



External SSA

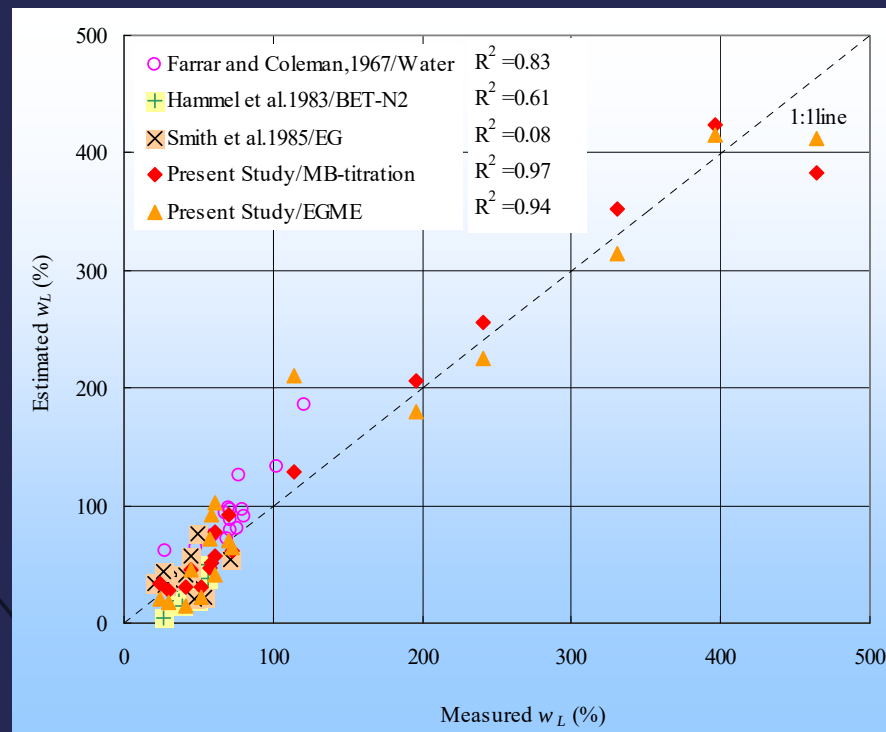


SSA and Atterberg limits relationship

Liquid limit can be estimated from SSA.

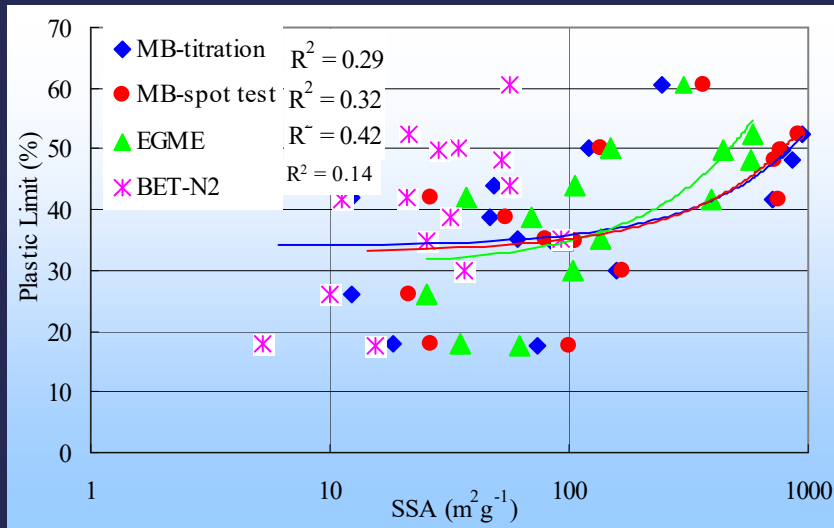
$$\text{SSA} = 2.37 w_L - 61.38 \quad (r = 0.98) \quad (\text{MB-titration})$$

$$\text{SSA} = 1.39 w_L + 6.2 \quad (r = 0.97) \quad (\text{EGME})$$

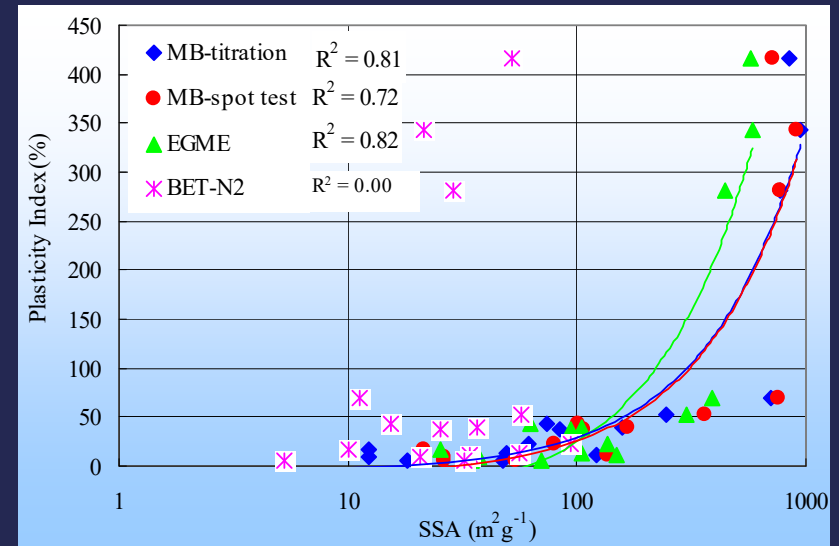


SSA and Atterberg limits relationship

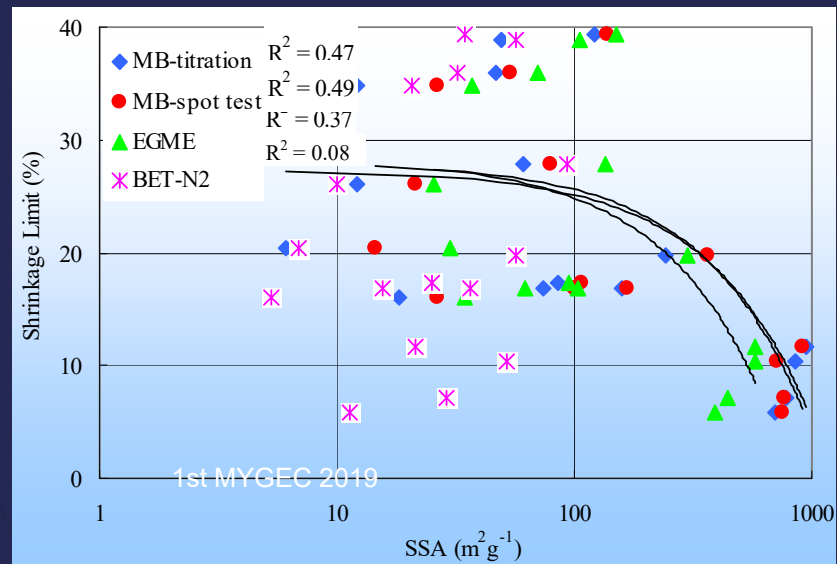
SSA versus Plastic limit



SSA versus Plasticity index

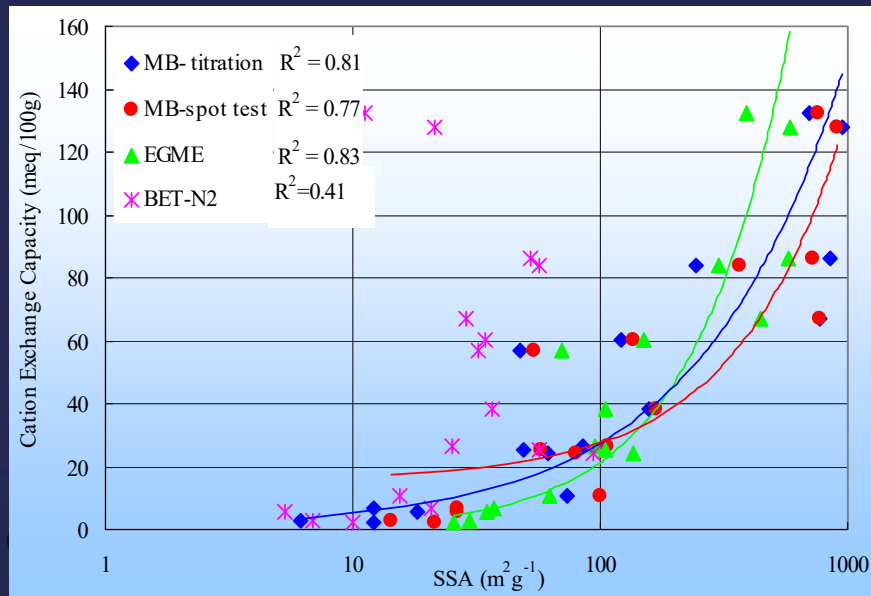


SSA versus Shrinkage limit

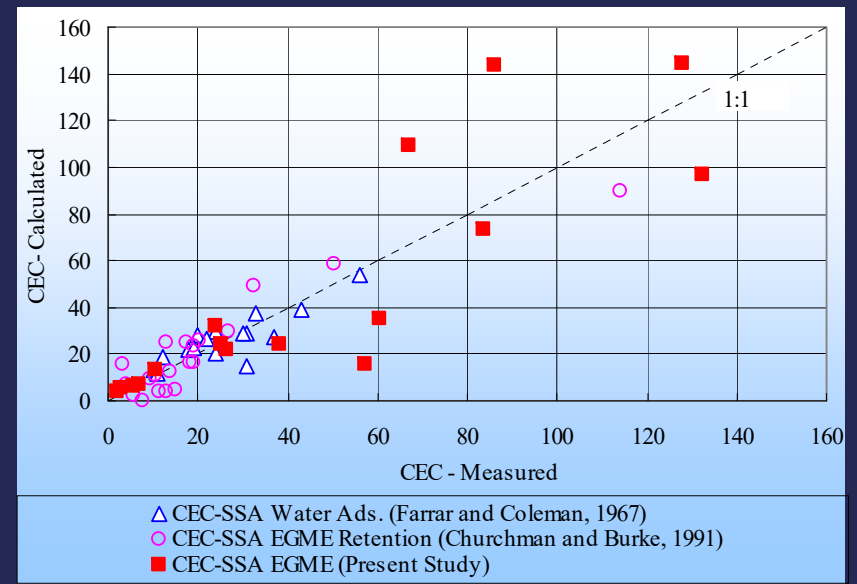


SSA and Cation exchange capacity relationship

SSA vs. CEC



Measured CEC vs. Calculated CEC



$$CEC = 0.91 \text{ SSA}^{0.74}$$

$$(r = 0.90)$$

(MB-titration)

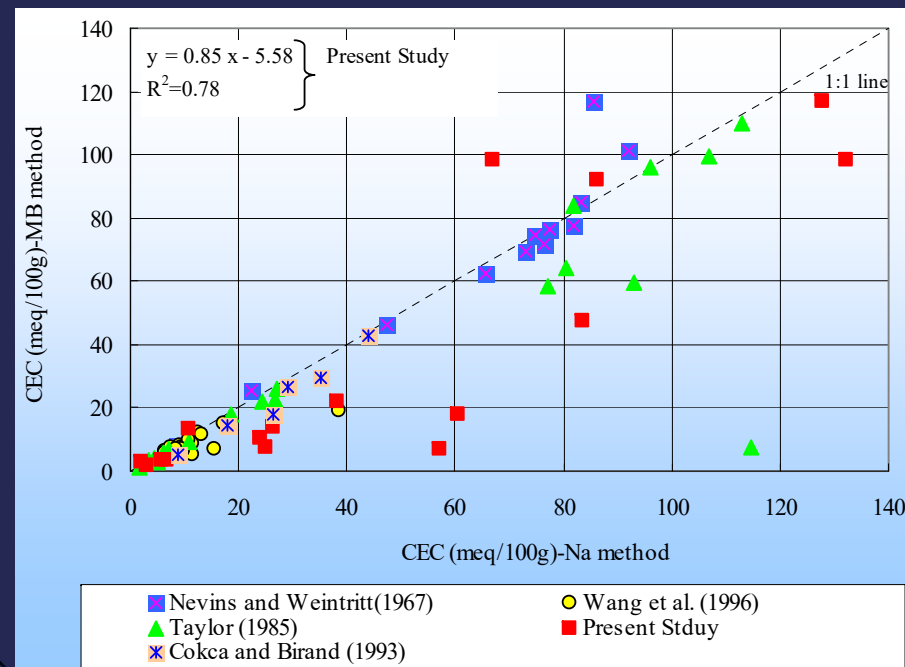
$$CEC = 1.114 \text{ SSA}^{1.14}$$

$$(r = 0.91)$$

(EGME)

SSA and Cation exchange capacity relationship

Comparison of Na-acetate and MB methods for determination of CEC:



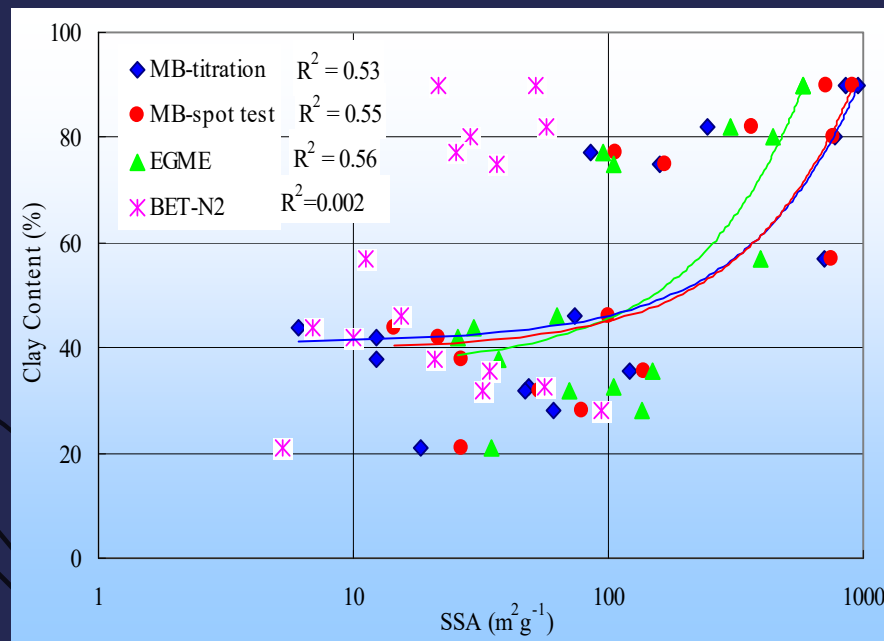
Cation exchange capacity can be determined by methylene blue test !!!

SSA and Clay content relationship

It is expected that as clay content increases, SSA of the soil increases.



But there is no general trend



SSA and Clay content relationship

SSA may not increase with clay content !!!



Clay content = 60 % (kaolinite)



SSA=60 m²g⁻¹

CC → High

SSA → Low



Clay content = 30 % (montmorillonite)



SSA=280 m²g⁻¹

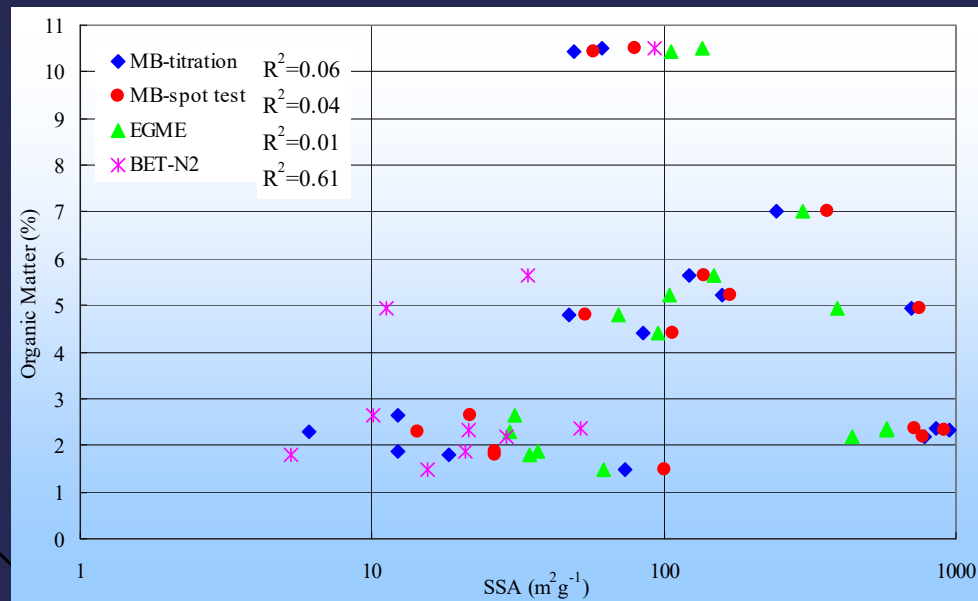
CC → Low

SSA → High

SSA and Organic matter relationship

SSA versus organic matter relationship :

There is no general trend !!!



SSA and Organic matter relationship

OM removal has minor effect on SSA that obtained by polar liquids!

Sample	Soil Organic Matter (%)	With organic matter MB-spot SSA	Without organic matter MB-spot SSA	Change in SSA after OM removal
R-1	10.4	57.6	24.5	Decrease 
R-2	2.3	14.4	12.2	Decrease 
R-3	1.9	26.4	30.6	No change 
R-4	2.7	21.6	48.9	Increase 
R-5	10.5	79.2	79.5	No change 
R-6	5.6	136.8	122.3	Decrease 
R-7	4.8	54.0	36.7	Decrease 
R-8	1.8	26.4	18.4	Decrease 
R-9	4.4	106.8	122.3	Increase 
R-10	1.5	100.8	79.5	Decrease 
R-11	7.0	364.8	464.9	Increase 
R-12	5.2	168.0	171.3	No change 
R-13	2.4	720.0	795.15	Increase 
R-14	5.0	753.6	734.0	Decrease 
R-15	2.2	768.0	850.2	Increase 
R-16	2.3	912.0	921.6	No change 

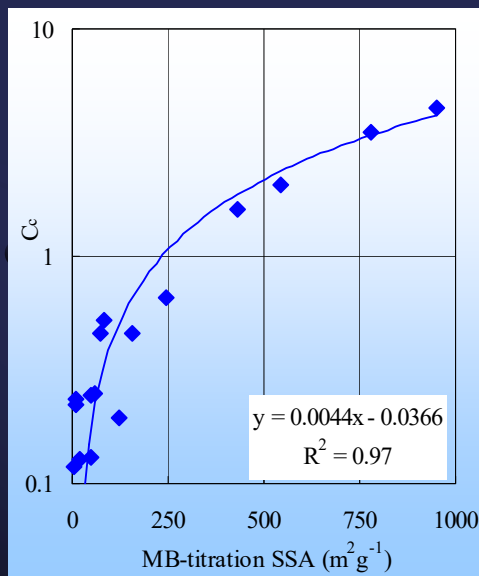
SSA and Compressibility Relationship

SSA versus Compression Index:

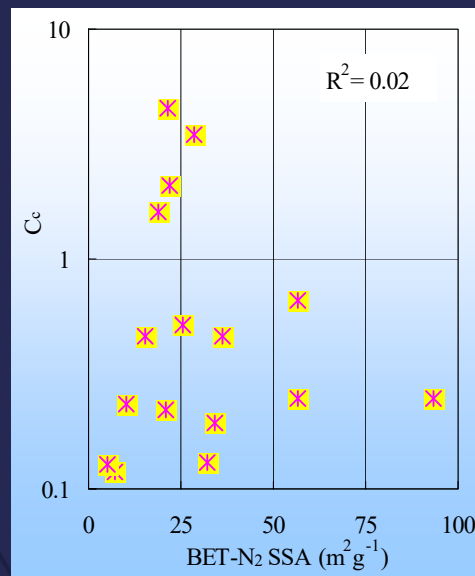
Compression index (C_c) increases as the SSA increases.

Remolded Samples

MB-titration SSA vs. C_c

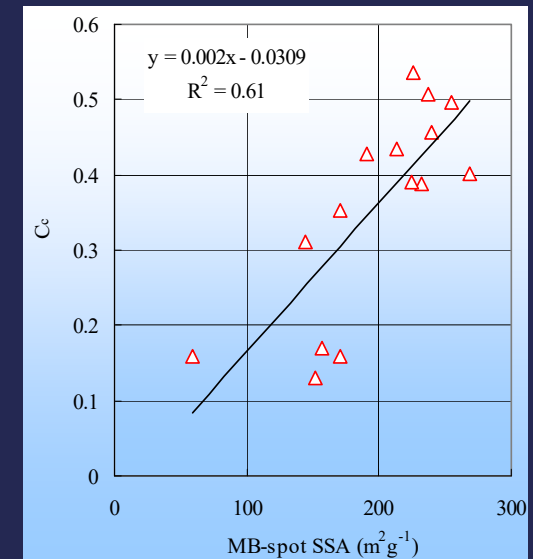


BET-N₂ SSA vs. C_c



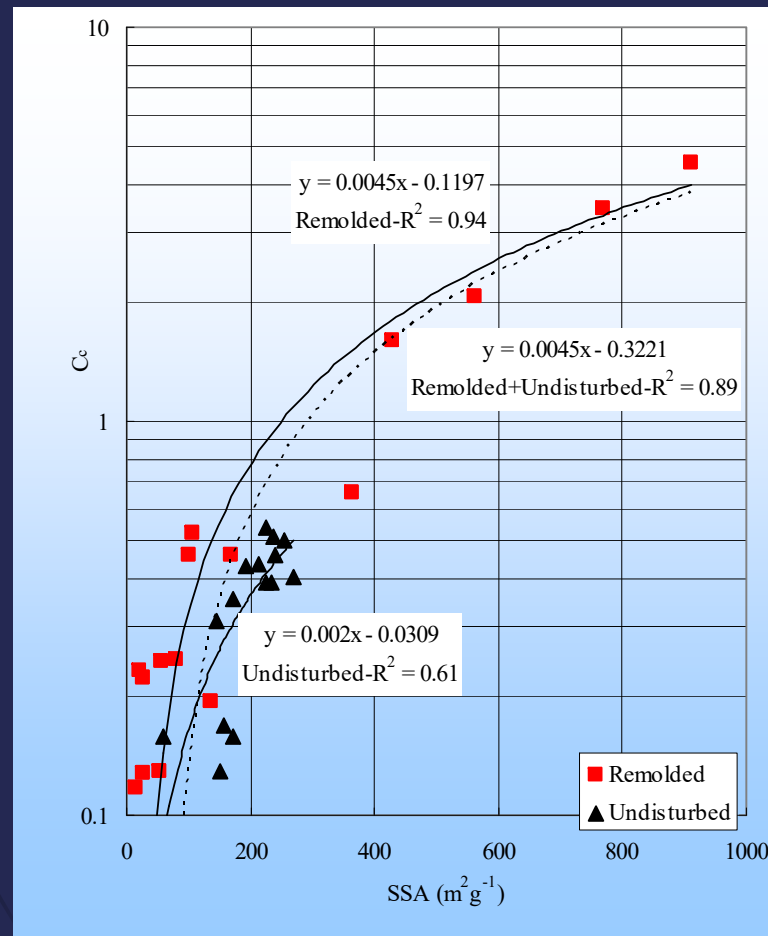
Undisturbed Samples

MB-titration SSA vs. C_c



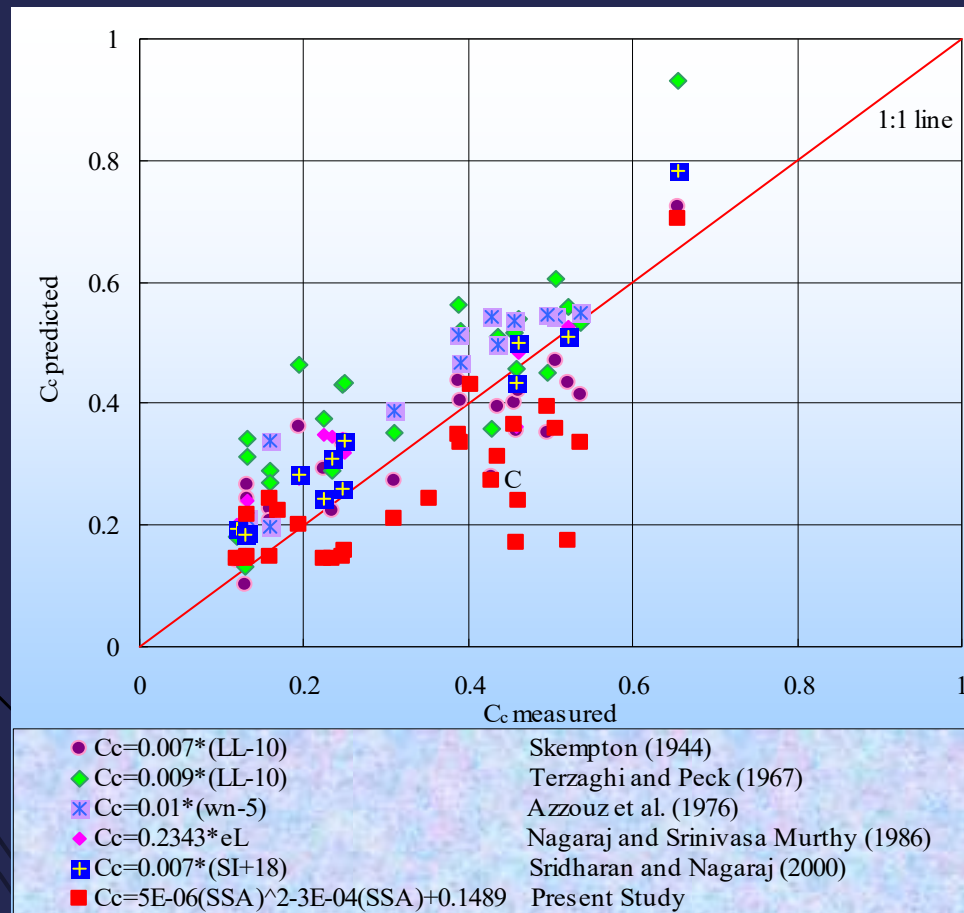
SSA and Compressibility Relationship

SSA versus compression index relationship for remolded and undisturbed samples:



SSA and Compressibility Relationship

Estimation of C_c from soil index properties and SSA !

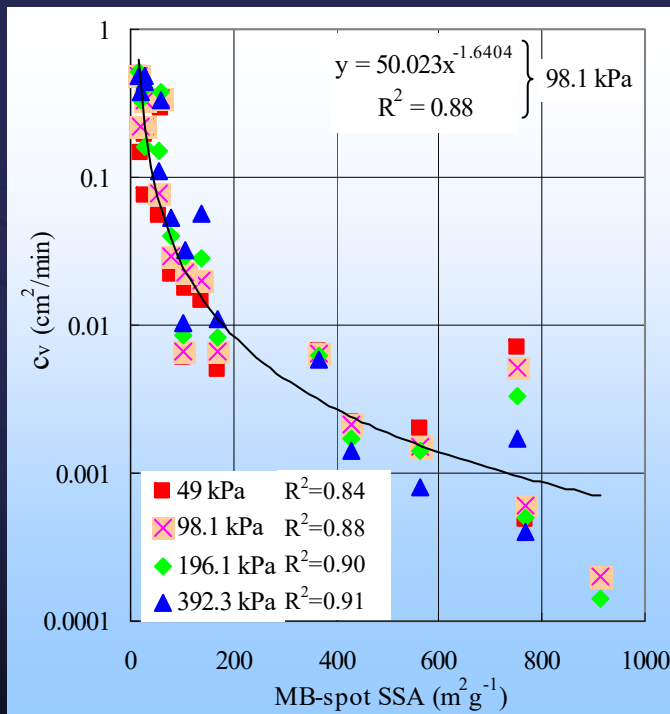


SSA and Compressibility Relationship

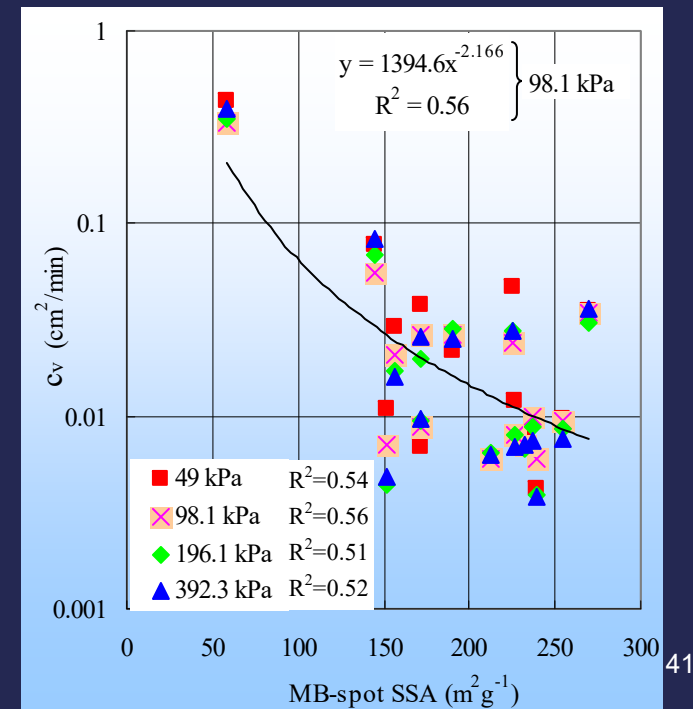
MB-spot SSA versus coefficient of consolidation (c_v):

Significantly high correlation coefficients between c_v and SSA $\Rightarrow$ especially for remolded samples

Remolded Samples



Undisturbed Samples



SSA and Swelling Relationship

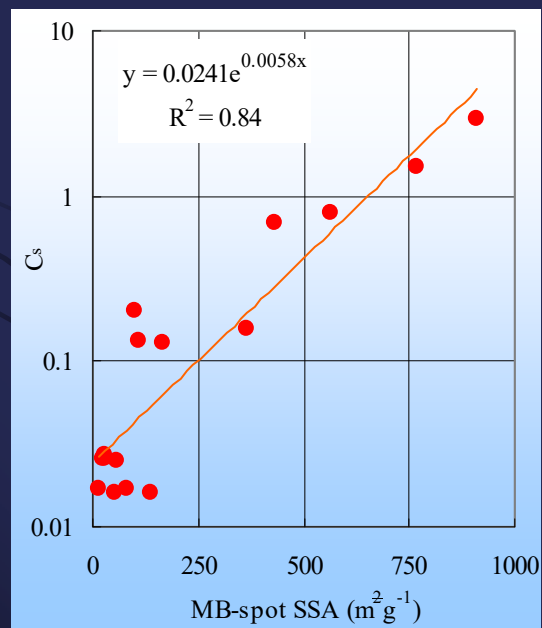
Swelling index determination methods:



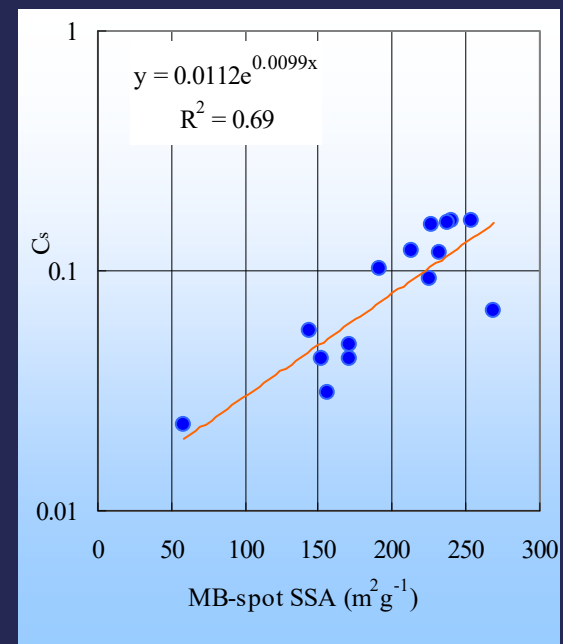
SSA and Swelling Relationship

Swelling index (C_s) versus SSA (from oedometer test):

Remolded Samples



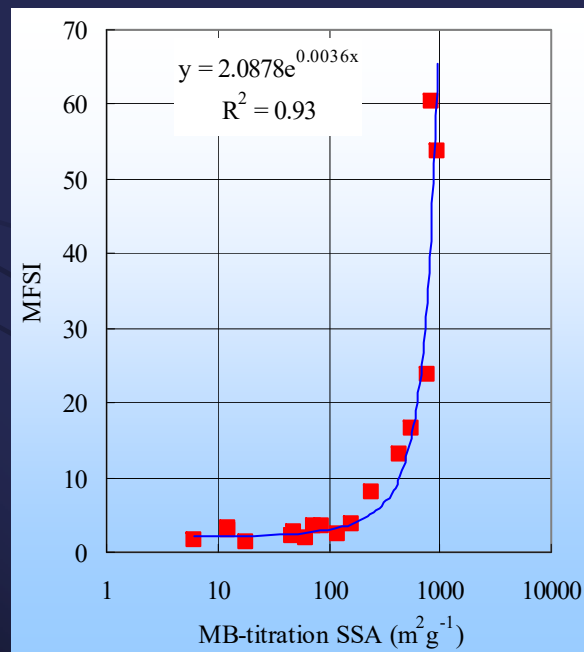
Undisturbed Samples



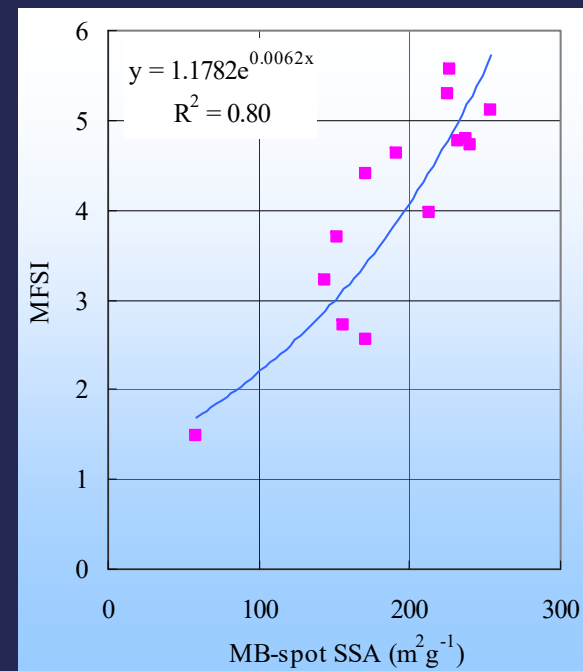
SSA and Swelling Relationship

Modified free swell index versus SSA:

Remolded Samples



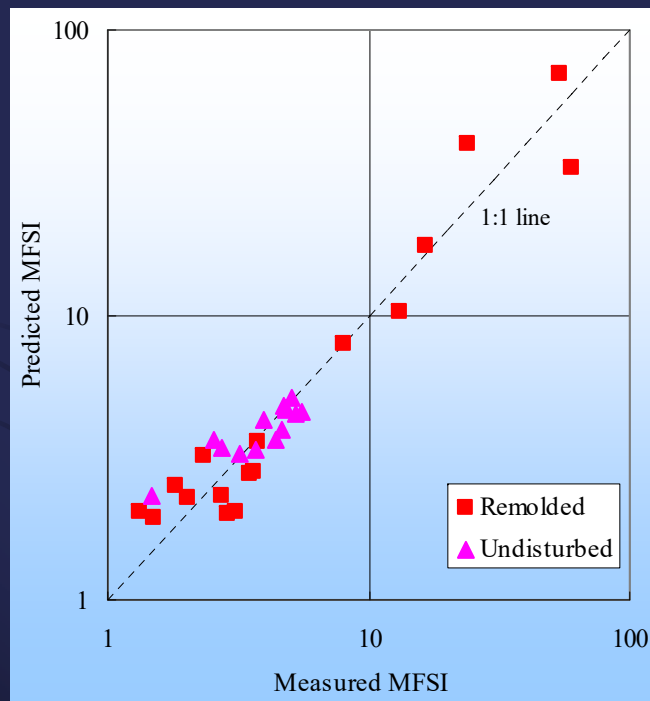
Undisturbed Samples



SSA and Swelling Relationship

Proposed prediction equation:

$$\text{MFSI} = 1.84 e^{0.004\text{SSA}}$$



Modified swell index
of the samples can be
estimated accurately
by simple methylene
blue spot test !

SSA and Swelling Relationship

Swelling potential estimation methods:

Swelling Potential					
Sample	MB-spot SSA (m ² g ⁻¹)	Dakshanamurthy & Raman (1973) (Based on w_L , I_p)	Van der Merve (1964) (Based on I_p , CC, A)	Holtz (1959) (Based on CC, I_p , w_s)	Isik (2006) (Based on w_L , CEC)
R-1	57.6	High	Low	Low	High
R-2	14.4	Low	Low	Low	Moderate
R-3	26.4	Medium	Low	Low	High
R-4	21.6	Medium	Low	Low	Moderate
R-5	79.2	High	High	Medium	High
R-6	136.8	High	Low	Low	High
R-7	54.0	Medium	Low	Low	High
R-8	26.4	Low	Low	Low	Low
R-9	106.8	High	Medium	Very high	High
R-10	100.8	High	Very high	Very high	High
R-11	364.8	Extra high	Very high	Very high	Very high
R-12	168.0	High	High	Very high	High
R-13	720.0	Extra high	Very high	Very high	Very high
R-14	753.6	Extra high	Very high	Very high	Very high
R-15	768.0	Extra high	Very high	Very high	Very high
R-16	912.0	Extra high	Very high	Very high	Very high

SSA and Swelling Relationship

A new classification is proposed for swelling estimation of the soils which is based on MB-spot SSA.

Specific Surface Area (m^2g^{-1})	Degree of Expansion
< 70	Low
70 – 150	Medium
150 – 300	High
300 – 400	Very high
> 400	Extra high

SSA and Permeability Relationship

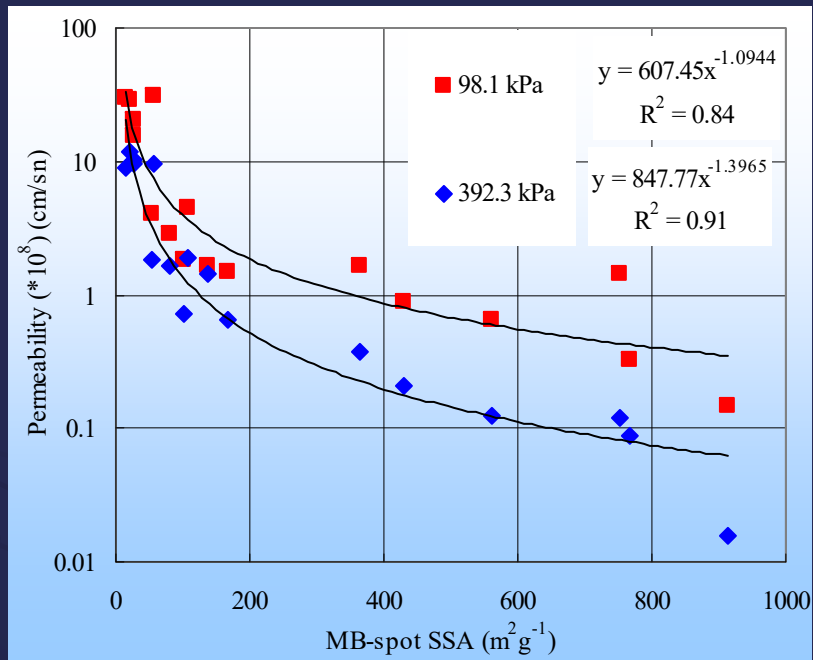
Kozeny-Carman equation relates the permeability and SSA.

$$k = 1.99 \times 10^4 (1/S_0^2) [e^3 / (1 + e)]$$

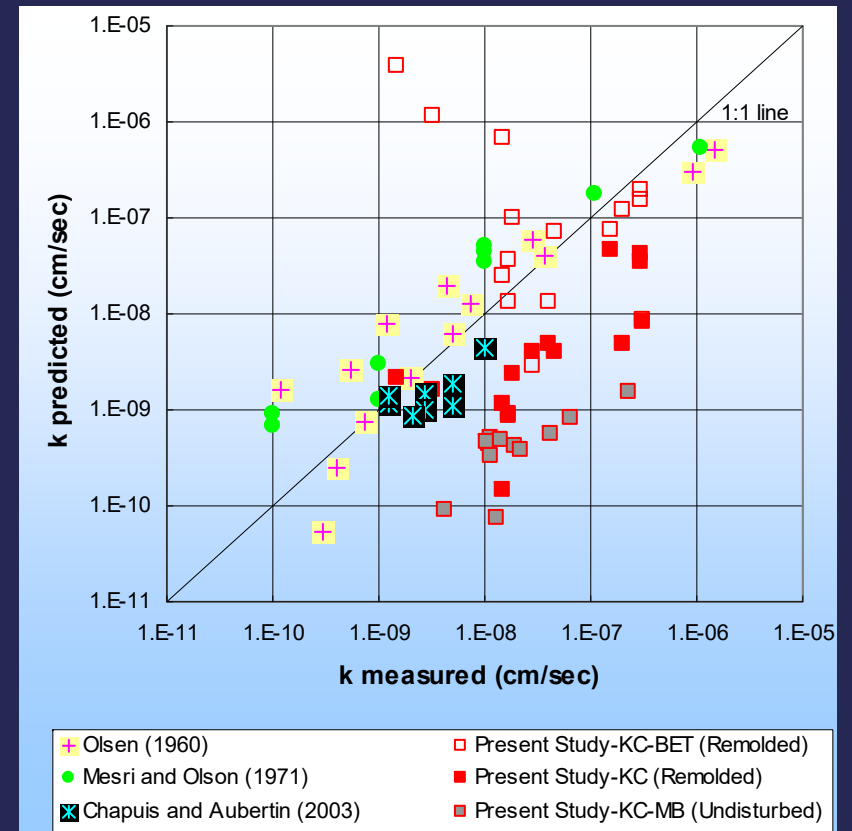
(at 20 °C) (Carrier III, 2003)

SSA and Permeability Relationship

MB-spot SSA vs. Permeability

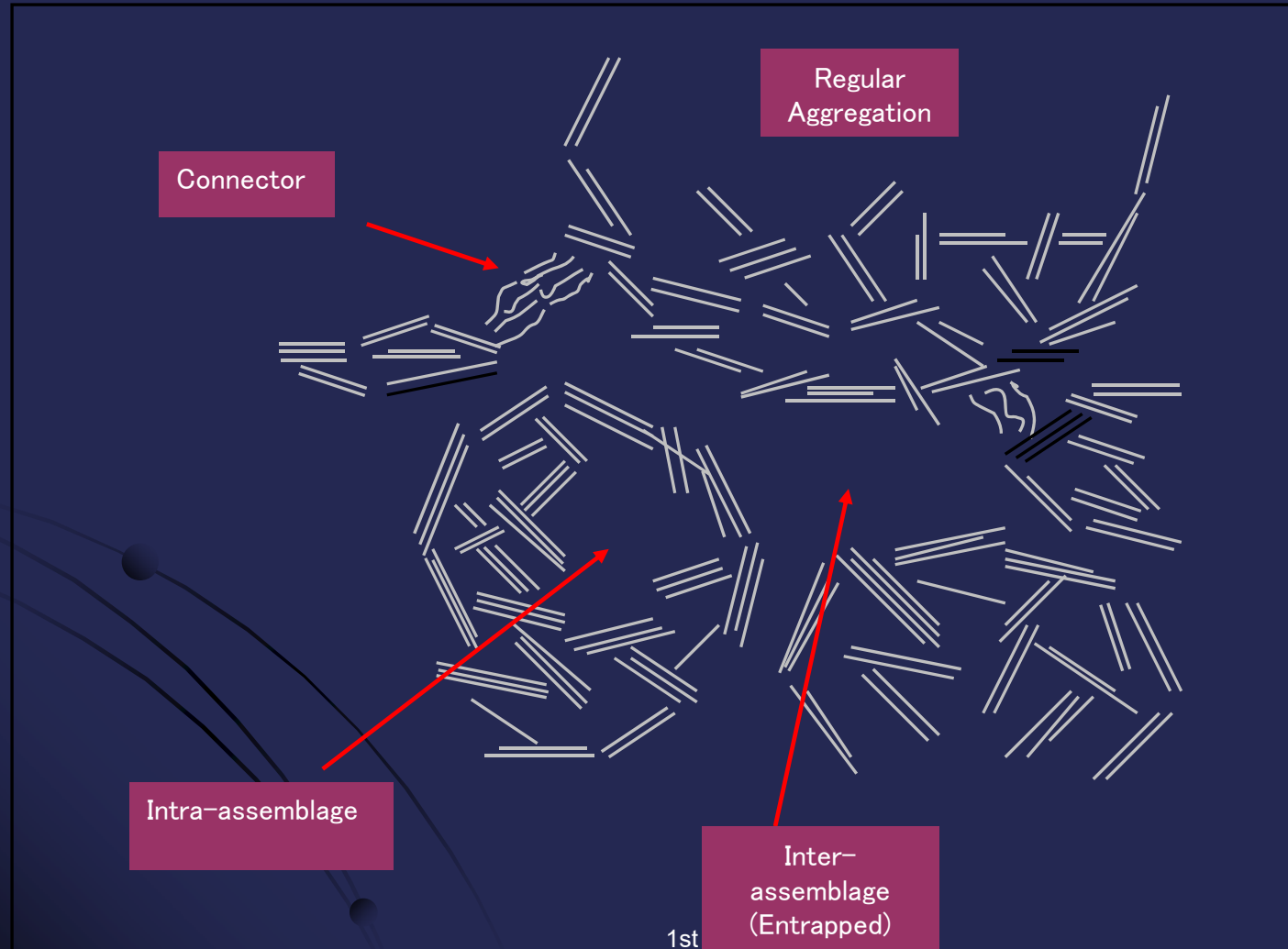
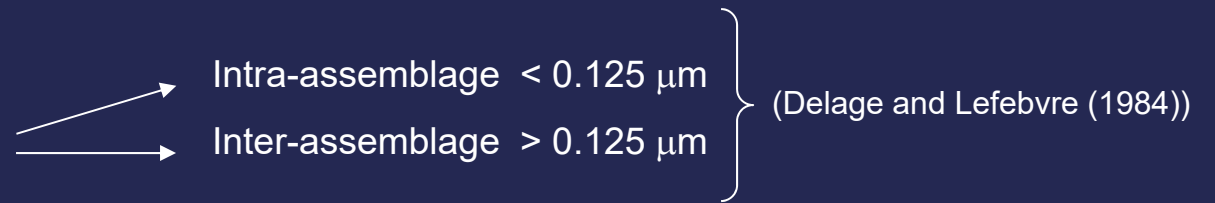


Permeability prediction by means of Kozeny-Carman equation



Pore Size Distribution

Pore classes



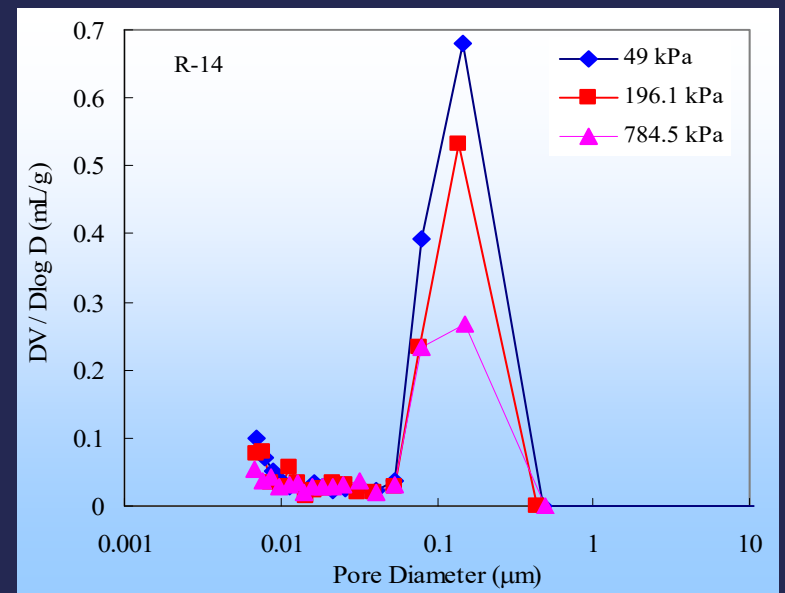
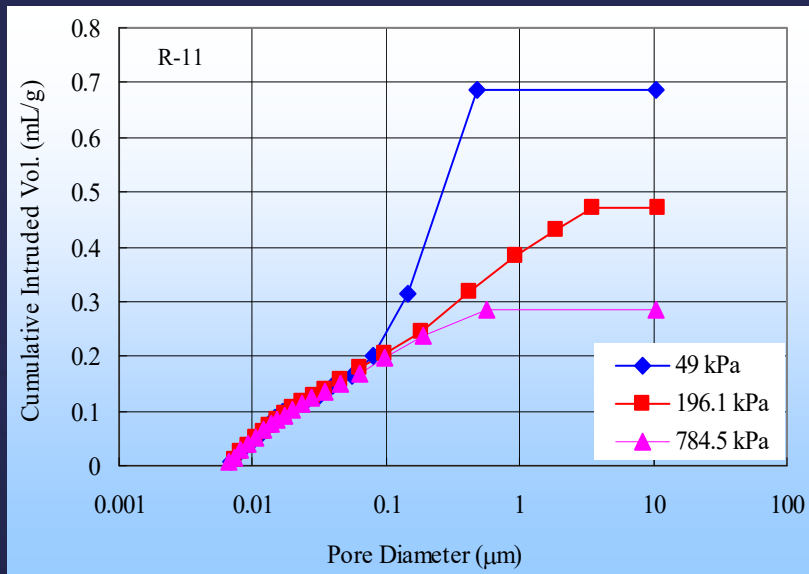
Pore Size Distribution

PSD is related;

- water, air, and heat conductivity properties;
- adsorption and desorption isotherms (capillary phenomena)
- volumetric deformation (rearrangements of fabric units).

Pore Size Distribution

Pore size distribution change with consolidation pressure:



Pore Size Distribution

- ✓ As consolidation pressure increases total intruded volume decreases.

Intra-aggregate pore size	→	No change
Inter-aggregate pore size	→	Decrease

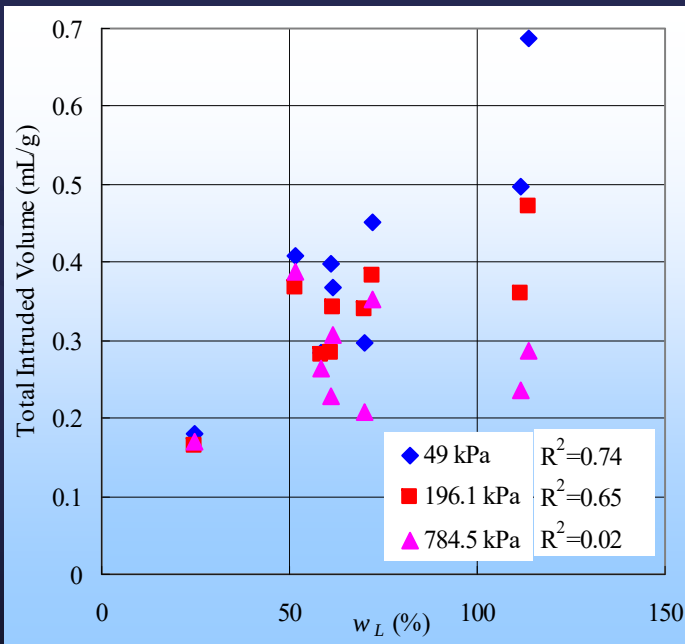


Pore Size Distribution

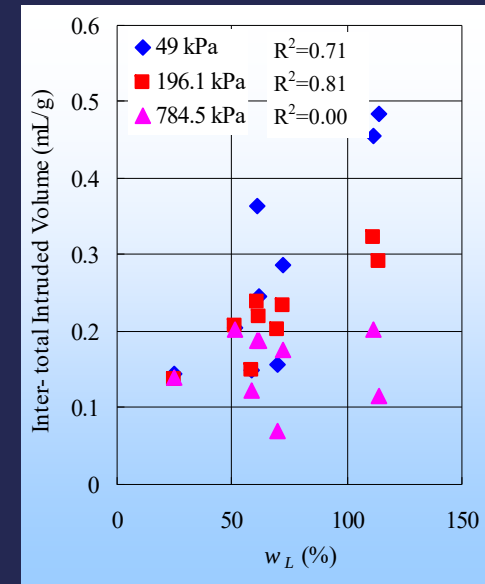
PSD not only dependent on consolidation pressure.

It also depends on inherent soil properties!!!

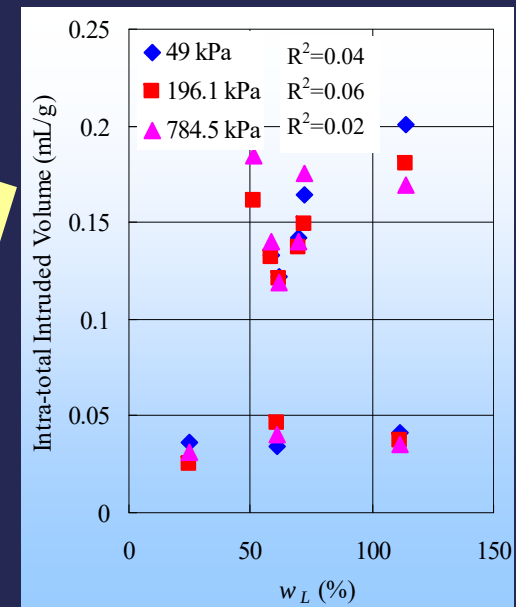
Total intruded volume versus liquid limit



Inter intruded volume



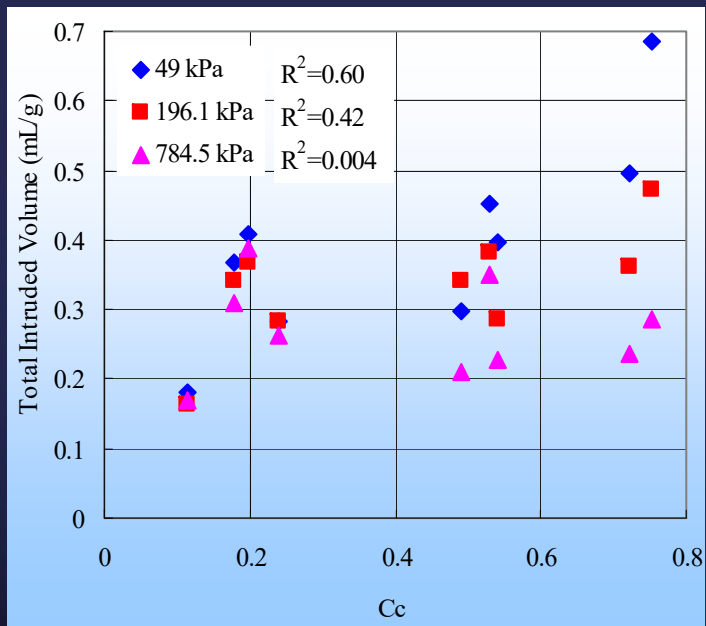
Intra intruded volume



Pore Size Distribution

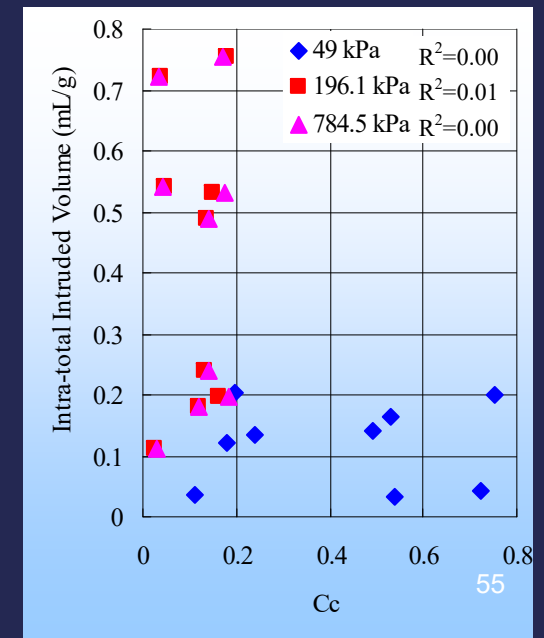
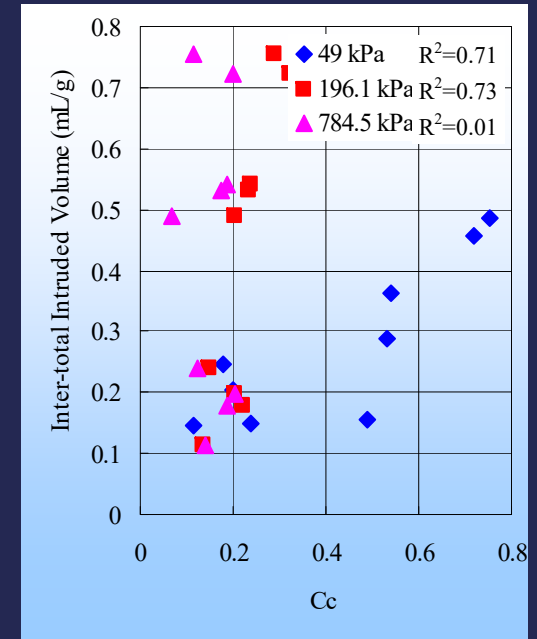
Pore size distribution versus compression index (C_c)

Total intruded volume versus C_c



Inter intruded volume

Intra intruded volume



Pore Size Distribution

PSD

have high correlation coefficients



- Liquid limit
- SSA
- Clay content
- Compression index
- Coefficient of volume compression



Pore Size Distribution

Scanning electron microscope (SEM) analysis

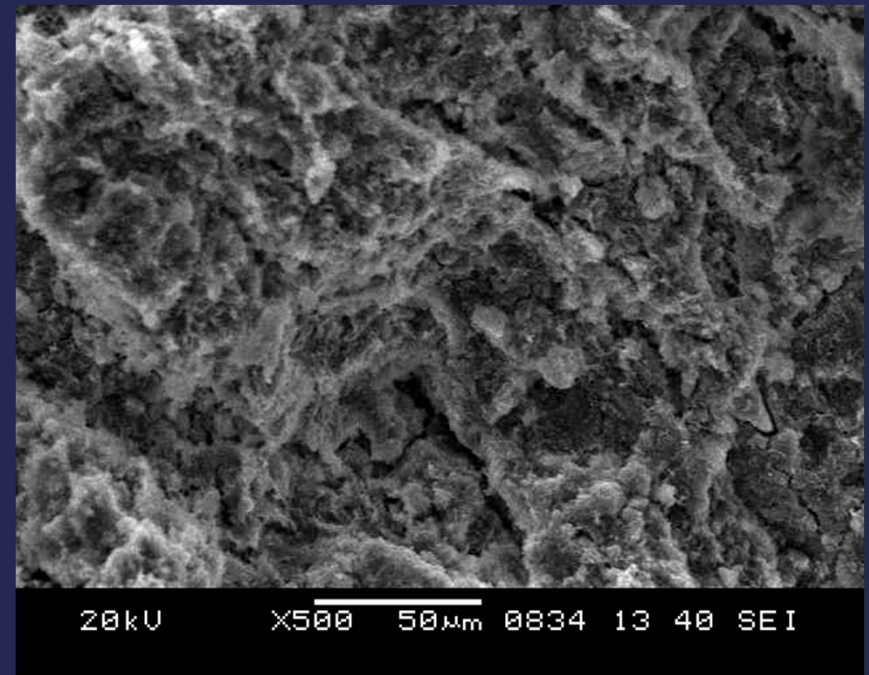
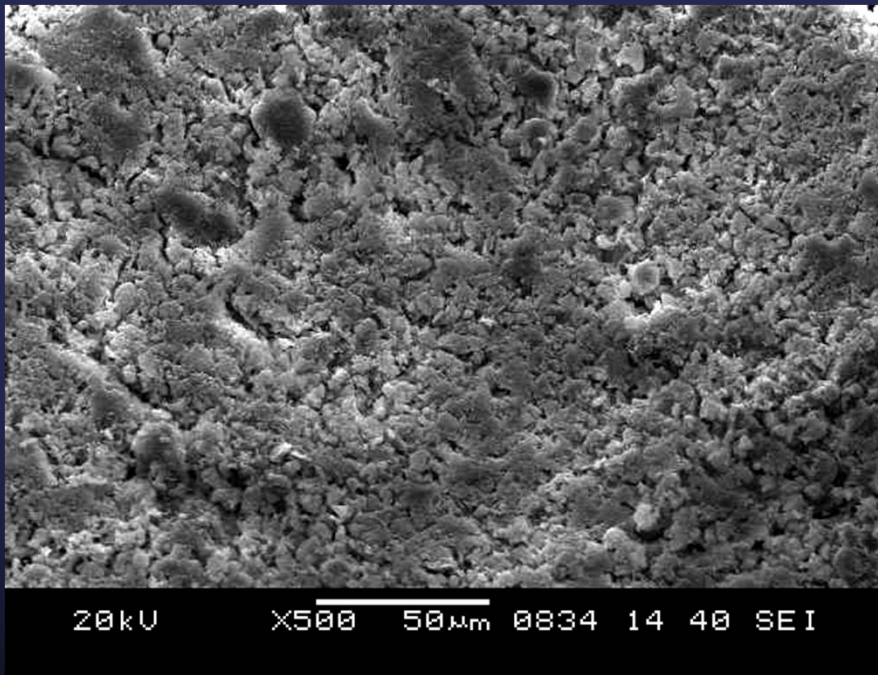
Pore size distribution of soils can be evaluated by SEM analysis!

Decrease in pore volume by consolidation pressure increment on R-11

49 kPa



784.5 kPa

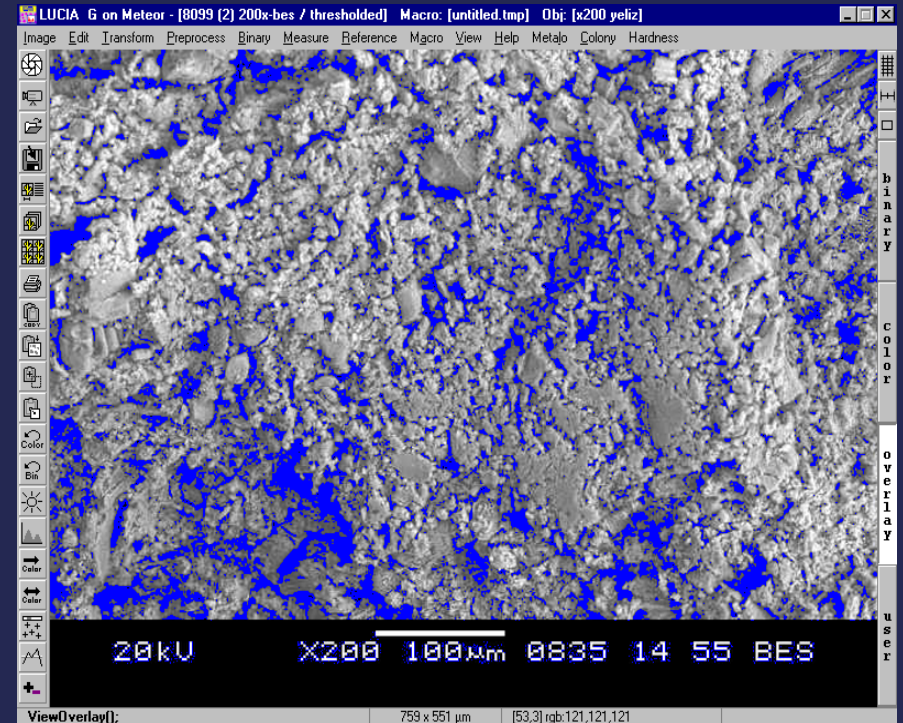
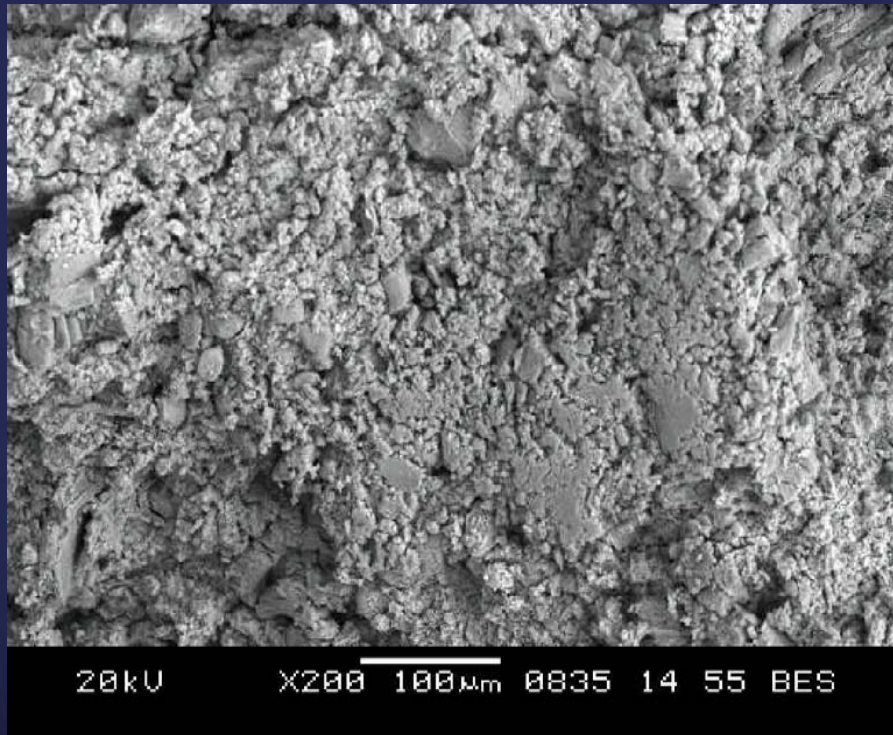


1st M **x500**

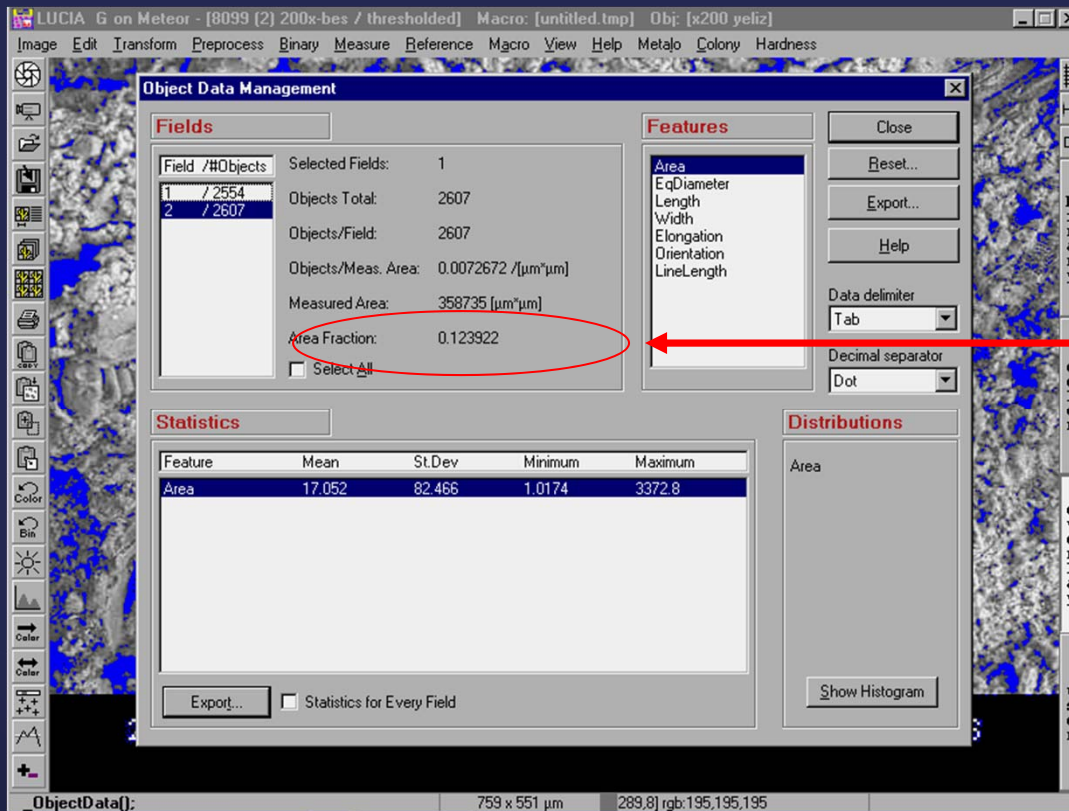
Results-Pore Size Distribution

Scanning electron microscope (SEM) analysis

Pore size distribution analysis by means of Lucia G (version 4.51) image analyzer program



Pore Size Distribution



Total pore area **12 %** of the sample according to image processing analysis

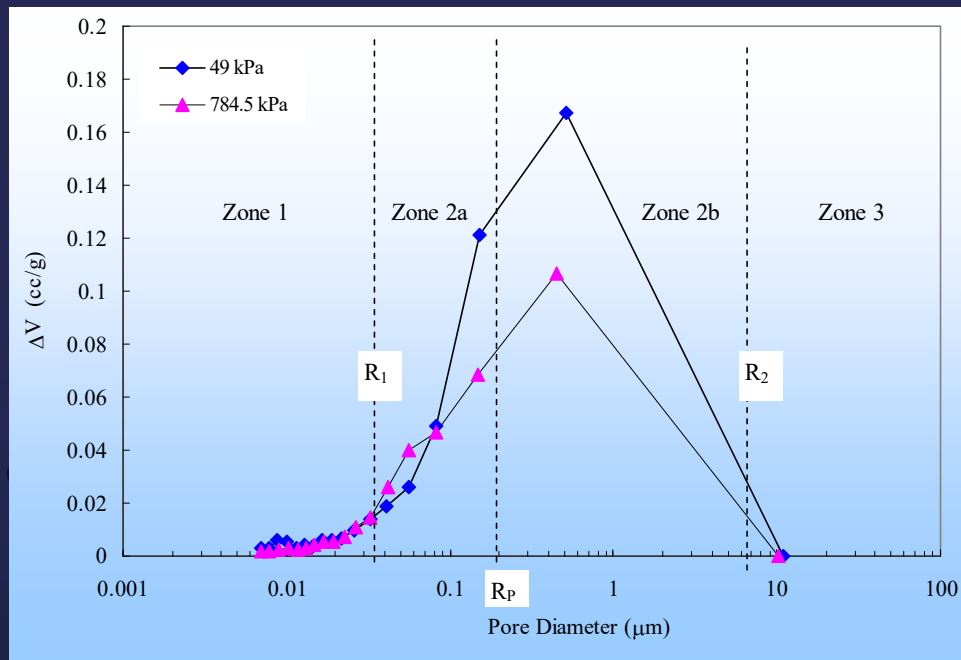


Total pore area **41 %** of the sample according to Mercury Intrusion Porosimetry test results

Pore Size Distribution

Mathematical modelling of PSD:

Pore size distribution modification of a structured soil subjected to increasing consolidation pressure can be estimated by mathematical modelling.

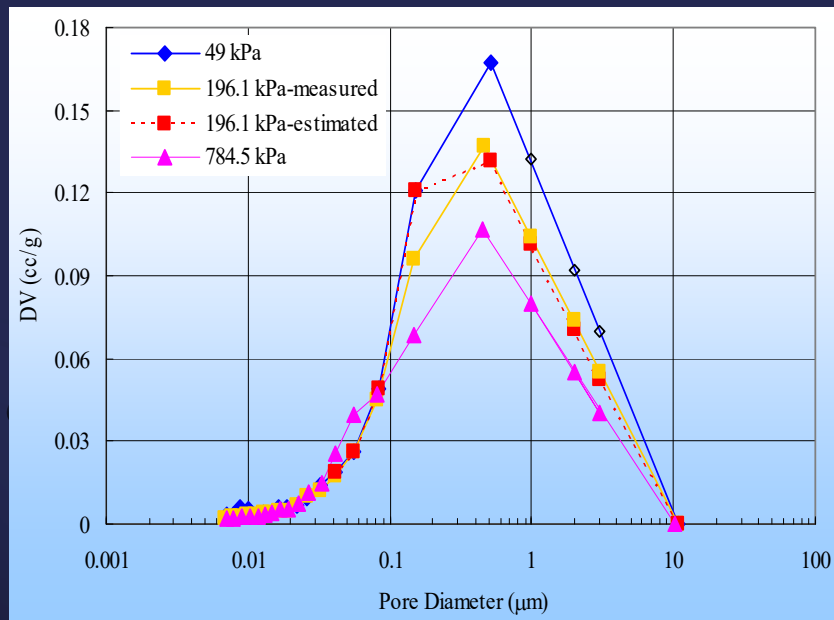


Zone 1 } Pores slightly affected
Zone 3 }

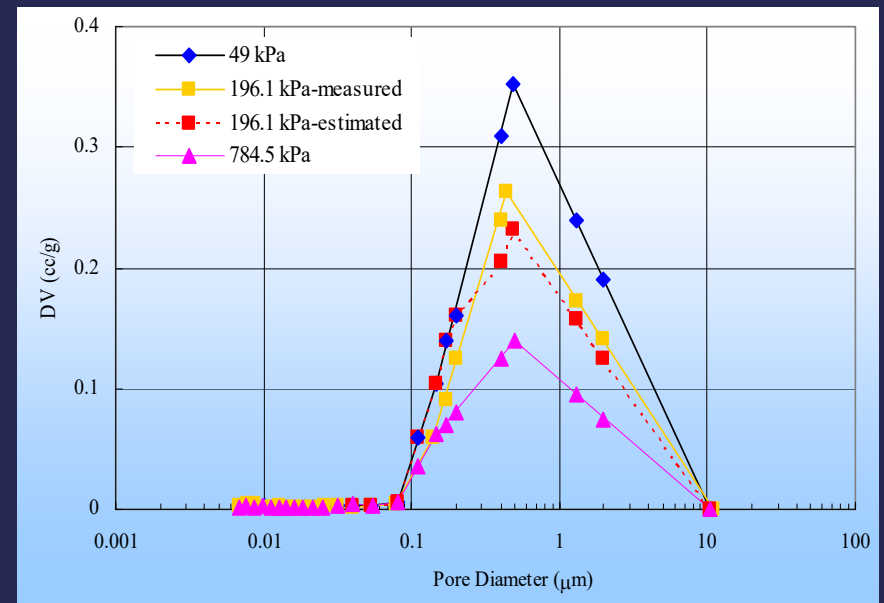
Zone 2 } Pressure influence domain

Pore Size Distribution

Mathematical modelling results of pore size distribution estimation:

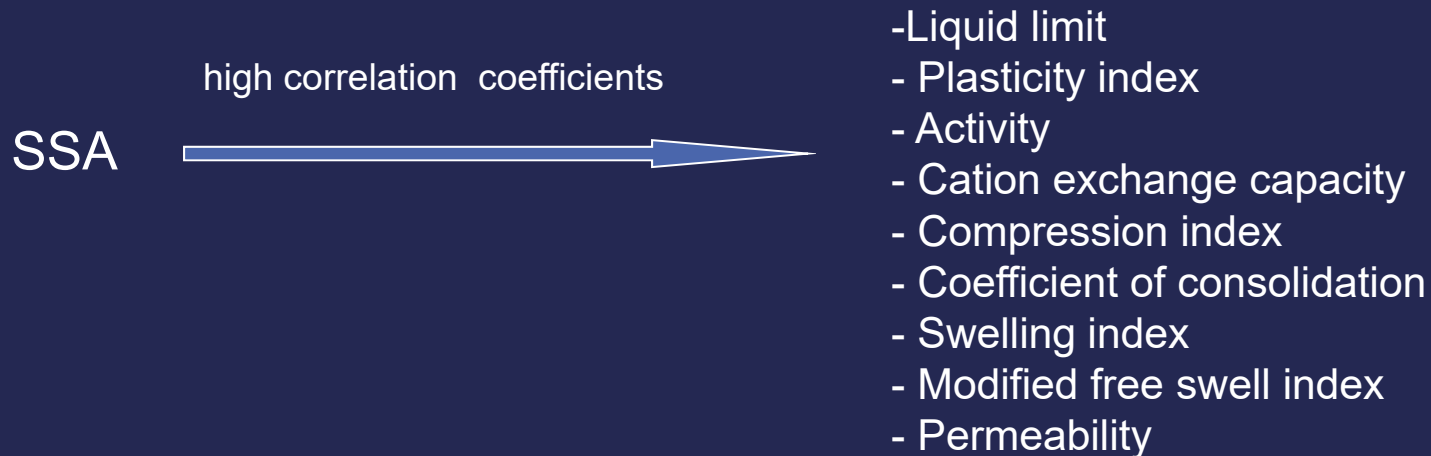


R-9



R-14

Conclusions – Specific Surface Area Effect on Engineering Properties of Soils



!!! When SSA is known $\rightarrow$ CEC, w_L , I_p , A, CEC, C_c , c_v , C_s , MFSI, k
can be estimated accurately !!!!

Conclusions – Pore Size Distribution

- The higher the consolidation stress, the lower the total intrusion volume.
- Inter-assemblage pores is responsible for deformation due to consolidation of soils.
- Not only consolidation pressure but also some inherent soil properties have effect on PSD.
- PSD have significant relationship with and liquid limit, clay content, and compression index.
- Pore volume analysis cannot be evaluated by Scanning Electron Microscope analysis, quantitatively.



THANKS
Questions are welcome!

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1st MYGEC 2019

