

CHAPTER II

LITERATURE REVIEW

2.1 Air-Permeability Method

The determination of specific surface area of packed particles was suggested independently by Carman and Dalla Valle²⁰ (1938), the technique developed has been known as permeametry. Permeametry indicates the surface area that contributes to the pressure drop when a fluid is made to flow through the packed particles. The flow may be either streamline or Knudsen flow. Obviously with streamline flow this surface area is the "noncontact" area over which the fluid passes and includes little of the area making up the walls of capillary cracks and pores within the body of porous particles. Streamline flow results indicate the external surface area of particles; they can be expected to correlate more or less closely with surface areas calculated from particle size measurements. With compacted beds of very fine particles and gases near atmospheric pressure or with coarse particles and gases at reduced pressure the ratio of mean free path of gases to capillary diameter of packed particles approached unity (or less than unity), Knudsen found that the rate of gas flow is greater than given by Poiseuille's law (Streamline flow). The effect is regarded as a "slip" at the capillary walls and the flow is called Knudsen flow. Lea and Nurse¹⁶ (1939) early realized the possibilities of the air permeability method and designed their apparatus for cement testing. By a slight

variation of the arrangement of apparatus, Gooden and Smith¹³ (1940) were able to incorporate a self-calculating chart which enabled specific surface or surface area diameter to be read off directly. Rigden^{24, 25} and Blaine^{2, 3} independently introduced the type of their apparatus for specific surface measurement of fine particles. Blaine's method is more rapid and if carefully used, this method give the results as accurate as the absorption method. It is now adopted for portland cement specifications in several countries.

2.2 Gas-Adsorption Method

In order to satisfy the resulting unbalance of atomic and molecular forces, the surface molecules attract gas, vapor or liquid molecules. If the molecules attracted are those of a gas, the phenomenon is known as gas adsorption. Gas adsorption measurements provide the best means for determining the total surface area. Basically, gas adsorption techniques involve a determination of the quantity of gas necessary to form a monomolecular layer on the surface to be measured. The number of molecules required to form this layer may be evaluated, and since the area occupied by each molecule is known (or may be estimated), the surface area of the material may be calculated. There are two process (a physical and a chemical process) involving in the adsorption phenomena depending on the system and the temperature employed. Physical adsorption (frequently referred to as Van der Waals' adsorption) is the result a relatively weak interaction between solid and gas. Almost all the gas adsorbed can be removed by evacuation at the same temperature at which it was adsorbed. Chemical adsorption or chemisorption is also an interaction

between solid and gas but is stronger than physical adsorption; evacuation at the elevated temperature is required for even partial removal. For the purpose of determining surface area, physical adsorption is required.

C.W. Sheele²⁰ (1773) first described that gases were taken up or adsorbed by charcoal. Beginning in 1914 theories based on an intermolecular potential gradient were proposed by Eucken and Polanyi. Langmuir²⁰ (1918) considered adsorption to be a chemical process and assumed that molecules are adsorbed in a monolayer only. At relatively low temperatures and at pressures approaching the saturation value, agreement of experimental data with Langmuir's theory is generally poor. At these conditions it is believed that adsorbed molecules can hold other gas molecules forming multimolecular layer. Brunauer, Emmett, and Teller^{1,20} (1938) therefore undertook to develop a unified theory of physical adsorption. The result is known as BET theory, from the first letter of each surname. The fundamental assumption of this theory is that the forces active in the condensation of vapors are also responsible for the binding energy in multimolecular adsorption. The BET method, using nitrogen gas as the adsorbate at the temperature of liquid nitrogen, has proved to be a very reliable means for determining the total surface area of powdered materials.

2.3 Relative Merits of Adsorption and Permeability Methods

The adsorption method is well suited to a research laboratory but, for routine work, a permeability method is simple, portable and easy to operate. The nitrogen adsorption surface is the value calculated from nitrogen adsorption, assuming that an adsorbed nitrogen molecule occupies 16.2 Sq. \AA at -196°C . It is by no means

certain that this area is the same for all adsorbents (the solid), and the calculated surface is uncertain to this extent. An advantage of the adsorption method is that it does not depend on pore texture, whereas the permeability method can only be applied if the pore texture is sufficiently random and uniform for the Kogeny equation to be valid. The equation describing the flow of a fluid through a bed of divided material was given by Kogeny in 1927. The general Kogeny equation was written as :

$$\frac{v}{t} = \frac{AAP}{Kn\lambda So^2} \frac{\epsilon^3}{(1-\epsilon)^2}$$

The consequences in relation to two method can be summarized briefly:

- a) The permeability method cannot be applied to consolidated media. (Even if it happens to give the correct surface, there is no means of knowing this without an independent value by the adsorption method.)
- b) While the permeability method does not require particles of uniform size, an excessively wide distribution of size should be avoided.
- c) The permeability method requires a carefully packed and uniform bed. This is easily attained with particles larger than 5μ , so that, for "coarse" particles, the permeability method readily yield accurate results, and is to be preferred to the adsorption method for both research and routine determinations. Fibrous particles, however, require great care in packing to give a uniform bed, and flat particles, e.g. mica, are unlikely to give trustworthy values. For particles below 5μ , aggregation due to surface forces becomes a factor of increasing importance. It can be overcome to some extent by compressing plugs to a porosity of somewhat under 0.5, but, even

then, as will be noted later, the permeability method still tends to give somewhat lower results than by nitrogen adsorption.

d) The adsorption method measures total accessible surface. The permeability method measures surface available to flow. Generally, however, the permeability measurement is the less significant, since only for rather coarse particle do surface roughness and the permeability of porous particles have a negligible influence on the total flow rate.

e) The adsorption method is not well suited to particles above 1μ , since the surface is too small for appreciable adsorption to take place.

2.4 Application of Both Method with Soils.

F.M. Lea and R.W. Nurse¹⁶ (1939) determined the specific surface of sand by air-permeability method and compared with water-permeability methods. The specific surface of some clay minerals such as Kaolinite, Attapulgus clay and Halloysite were determined with nitrogen adsorption method and compared with permeability method by J.M. Dalla Valle and Clyde Orr, Jr.^{5,20} (1950) but the results were more different. The air-permeability apparatus, based on normal Kozeny-Carman equation, such as Blaine air-permeability, can be used to determine the surface area of particle size down to 5μ in diameter and the air-permeability apparatus based on modified Kozeny-Carman equation, such as the modified Pechukas and Gage²² apparatus, can be used to measure the surface area of particle size down to 0.1μ in diameter. The nitrogen adsorption method is not well suited to particles size above 1μ in diameter. Therefore, coarse grained soil and some fine grained soil can be determined by air-permeability method and most of fine grained soil can be determined by nitrogen adsorption method.

2.5 Investigated Procedure

The investigated procedure was divided into 3 stages as following:

Stage 1 For sand size sample

The sample was first washed with clean water, then a deflocculating agent (sodium silicate) was added to the mixture. A spoon or glass rod were used to stir the slurry. The slurry was washed through No. 80 sieve and the finer particle was oven dried. The dried sample was powdered and passed through a following set of sieves No.80, No.100, No.140, No.200, No.270 and No.400. The weight of the soil retained on each sieve were measured and the percentages of retaining were calculated. The prepared soil samples was tested with the apparatus having 2.0 c.m. diameter glass tube.

Stage 2 For silt size sample

The grain size distribution of the soil sample, passing through No.200, sieve, was recorded by hydrometer method and the sample was tested with the apparatus having 0.80 c.m. diameter glass tube.

Stage 3 For clay size sample

The type and quantity of clay minerals in soil sample was determined by x-ray diffraction method. Applying the Stoke's law, the time for sedimentation of the soil particles, having larger size than clay size ($>2\mu$), was calculated.

The suspended clay size particle was separated from the other sedimented particles and oven dried. The prepared samples were tested with the apparatus having 0.40 c.m. diameter glass

tube. The time for the sedimentation of the soil particle having larger size than clay size particle were calculated as follow:

From the Stoke's law

$$D = \sqrt{\frac{1800 \eta \cdot H}{G - G_w \cdot t}}$$

Where D = Diameter of grain in m.m.

η = Viscosity of liquid in $\frac{\text{gm-sec}}{\text{c.m.}^2}$

G = Specific gravity of soil grains

G_w = Specific gravity of liquid

H = Height of falling in c.m.

t = Time in second

$$\text{If } D = 2 \times 10^{-3} \text{ m.m., } \eta_{23^\circ\text{C}} = \frac{0.00938}{980} \frac{\text{gm. -sec}}{\text{c.m.}^2}$$

$$G_w = 0.9976, H = 30 \text{ c.m.}$$

Substituting in Stoke's equation

$$2 \times 10^{-3} = \sqrt{\frac{1800 \times 0.00938 \cdot 30}{(G - 0.9976)980 \cdot t}}$$

$$t = \frac{0.129 \times 10^6}{G - 0.9976}$$

If $G = 2.739$ (Sample Pe 354)

$$t = \frac{0.129 \times 10^6}{2.739 - 0.9976} \text{ Sec.}$$

$$= 20.577 \text{ Hrs.}$$

If $G = 2.671$ (Sample 5992)

$$t = \frac{0.129 \times 10^6}{2.671 - 0.9976} \text{ Sec.}$$

$$= 21.413 \text{ Hrs.}$$

If $G = 2.687$ (Sample 674)

$$t = \frac{0.129 \times 10^6}{2.687 - 0.9976} \text{ Sec.}$$

$$= 21.211 \text{ Hrs.}$$

If $G = 2.712$ (Sample P_f 886)

$$t = \frac{0.129 \times 10^6}{2.687 - 0.9976} \text{ Sec.}$$

$$= 20.901 \text{ Hrs.}$$

Note Stoke's law is valid only for Reynold

nos. ($Re = \frac{vdf}{u}$) less than 0.5