



## Absolute method for determination of specific surface area using gas (air) permeability technique

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*New equation was derived for obtaining specific surface area from experimental data of gas flow through packed beds of porous materials. Preliminary experimental data for cement sample using the enhanced PV-Pyc 200 pycnometer setup yield good results.*

In the previous article entitled: "Proposal of quadratic equation for prediction of flow rates versus pressure in packed beds of cement", the following quadratic equation was proposed:

$$\text{Flow rate [Volume/time]} = F = a \cdot (P^2 - P_{ref}^2) \quad (\text{Eq. 1})$$

where **P** is the pressure at the input (top) of the packed bed, **P<sub>ref</sub>** is the pressure at the exit from the packed bed, and the coefficient **a** is a constant. In majority of practical applications, the **P<sub>ref</sub>** is the atmospheric pressure, or close to it, although different setups may use either a certain vacuum level or some pressure above atmospheric.

In addition to the comparative approach of evaluating specific surface area of cement or other porous powders by using reference materials in the mentioned article, the attempt is made here to provide an absolute method for determination of specific surface area from permeability measurements.

The above equation is similar to the well-known and referred to as Poiseuille equation corrected for compressible fluids (gases):

$$Q \text{ [Volume/time]} = \pi \cdot R^4 / (16 \cdot \mu \cdot h \cdot P_o) \cdot (P^2 - P_o^2) \quad (\text{Eq. 2})$$

where:

**Q** - flow rate through a capillary [cm<sup>3</sup>/s]

**R** - capillary radius [cm]

**μ** - dynamic viscosity [Pa · s]

**h** - height (length) of the packed bed [cm]

**P** - pressure at the packed bed entrance [kPa]

**P<sub>o</sub>** - pressure at the exit from packed bed (same as **P<sub>ref</sub>**) [kPa]

Let **S<sub>a</sub>** [cm<sup>2</sup>/g] be the surface area per unit of mass that we try to find out using experimental results of flow rates versus pressure differential across a packed bed. Let us assume, that the flow rate through a packed bed can be represented by the same flow rate but through **N** capillaries, and each capillary having the same (representative, equivalent) radius **R** and length **h** (same as the bed height). The total area of all capillaries can be calculated as:

$$S_a \cdot m_b = 2 \cdot \pi \cdot R \cdot h \cdot N \quad (\text{Eq. 3})$$

where **m<sub>b</sub>** is the mass of the packed bed of powder. Since the specific surface area is expressed in units of area per unit of mass, the value of **S<sub>a</sub>** is multiplied by the mass of bed to produce the total area. This equation can be rearranged to a simpler form for further manipulations as

$$\underline{\mathbf{N} \cdot \mathbf{R}} = \mathbf{S}_a \cdot \alpha \quad (\text{Eq. 4})$$

where

$$\alpha = \mathbf{m}_b / (2 \cdot \pi \cdot \mathbf{h}) \quad (\text{Eq. 5})$$

Since the Eq. 2 can be used to calculate flow rate through a single capillary, the suffix 1 can be used to identify such flow rate as  $\mathbf{Q}_1$ . Experimentally, only the total flow  $\mathbf{F}$  through all capillaries is measured. Multiplying both sides of Eq. 2 by  $\mathbf{N}$ , and since  $\mathbf{N}$  times  $\mathbf{Q}_1$  is equal to  $\mathbf{F}$ , the equation 2 becomes:

$$\mathbf{F} = \mathbf{N} \cdot \pi \cdot \mathbf{R}^4 / (16 \cdot \mu \cdot \mathbf{h} \cdot \mathbf{P}_o) \cdot (\mathbf{P}^2 - \mathbf{P}_o^2) \quad (\text{Eq. 6})$$

In order to combine known quantities and separate them from unknowns  $\mathbf{N}$  and  $\mathbf{R}$ , the equation can be written as:

$$\underline{\mathbf{N} \cdot \mathbf{R}^4} = \beta \quad (\text{Eq. 7})$$

where

$$\beta = (16 \cdot \mu \cdot \mathbf{h} \cdot \mathbf{P}_o \cdot \mathbf{F}) / (\pi \cdot (\mathbf{P}^2 - \mathbf{P}_o^2)) \quad (\text{Eq. 8})$$

The third equation that is needed in order to determine three unknowns:  $\mathbf{S}_a$ ,  $\mathbf{N}$ ,  $\mathbf{R}$ , can be provided by stipulating that the total surface area of all capillaries should be equal to bed area corrected by porosity factor  $\epsilon$ , as the "empty" area available for flow. Therefore,

$$\pi \cdot \mathbf{R}^2 \cdot \mathbf{N} = \mathbf{A}_b \cdot \epsilon \quad (\text{Eq. 9})$$

where  $\mathbf{A}_b$  is the area of the packed bed.

Again, the Eq. 9 can be rearranged to simplify manipulations as

$$\underline{\mathbf{N} \cdot \mathbf{R}^2} = \gamma \quad (\text{Eq. 10})$$

where

$$\gamma = \mathbf{A}_b \cdot \epsilon / \pi \quad (\text{Eq. 11})$$

The set of three equations, 4, 7, and 10, is easy to solve. Multiplying Eq. 4 by  $\mathbf{R}$ , and subtracting Eq. 10 from it, the value of  $\mathbf{R}$  can be expressed as

$$\mathbf{R} = \gamma / (\alpha \cdot \mathbf{S}_a) \quad (\text{Eq. 12})$$

Multiplying Eq. 10 by  $\mathbf{R}^2$  and subtracting it from Eq. 7, it yields

$$\mathbf{R}^2 = \beta / \gamma \quad (\text{Eq. 13})$$

Squaring Eq. 12 and subtracting Eq. 13 from it, it allows expressing the specific surface area  $\mathbf{S}_a$  as

$$\mathbf{S}_a^2 = \gamma^3 / (\alpha^2 \cdot \beta) \quad (\text{Eq. 14})$$

After carrying out the algebra, the  $\mathbf{S}_a$  can be expressed in known quantities as

$$\mathbf{S}_a = \{(\mathbf{A}_b^3 \cdot \epsilon^3 \cdot \mathbf{h} \cdot (\mathbf{P}^2 - \mathbf{P}_o^2) / (4 \cdot \mathbf{m}_b^2 \cdot \mu \cdot \mathbf{P}_o \cdot \mathbf{F}))\}^{1/2} \quad (\text{Eq. 15})$$

or in equivalent form

$$S_a = A_b / (2 \cdot m_b) \{ \epsilon^3 \cdot V_b \cdot (P^2 - P_o^2) / (\mu \cdot P_o \cdot F) \}^{1/2} \quad (\text{Eq. 16})$$

where:

$A_b$  - bed area

$\epsilon$  - bed porosity

$h$  - bed height (length)

$m_b$  = mass of sample used for the bed formation

$V_b$  - bed volume (geometrical)

$P$  - set input pressure (at the top of the cell)

$P_o$  - output pressure, usually atmospheric pressure

$F$  - flow rate

$\mu$  - dynamic viscosity [Pa·s]

The equations 15 or 16 do not use any additional factor(s) that would require either calibration or to have an assumed (accepted) value. It does not require any reference materials, as in a comparative approach. Therefore, in this sense, it can be considered as an absolute equation.

Similar assumptions of flow through a number of parallel capillaries were used in derivation of well known Carman-Kozeny equation. There are, however, some important differences between the Carman-Kozeny formula for the surface area calculations and Eq. 15. Among them, the term  $(1 - \epsilon)$  is not present in Eq. 15 and Eq. 15 uses  $(P^2 - P_o^2) / P_o$  instead of just  $P - P_o$ .

The value of the capillary radius,  $R$ , can be calculated either from Eq. 13 or by substituting the surface area  $S_a$  into Eq. 12. The flow through such a single capillary of radius  $R$  can be calculated from Eq. 2. The total number of capillaries,  $N$ , can be obtained by dividing the experimentally measured flow through packed bed,  $F$ , by the flow through a single capillary.

Using the PV-Pyc 200 pycnometer, the external cell assembly for housing the packed bed, and auxiliary hardware (bubble meter, digital stop-watch), the specific surface of any powdered substance can be easily determined. If the substance true volume (density) is not known, then it can be measured by using the pycnometer with standard equipment for regular volume (density) measurements. Once the true volume is known, it will be needed for calculating the porosity of the bed. The porosity,  $\epsilon$ , is a dimensionless quantity and is defined as

$$\epsilon = V_v / V_b = (V_b - V_p) / V_b = 1 - V_p / V_b \quad (\text{Eq. 17})$$

where  $V_v$  is void volume,  $V_b$  is geometrical volume of the formed packed bed, and  $V_p$  is the true volume of the bed determined by pycnometer.

The diameter of the cell is known and constant, but the height of the bed and the mass of sample used for the bed forming need to be recorded. With the external cell attached to the pycnometer, and pressure set, the flow rate measurements can be carried out. Entering all the data into the software, the dedicated calculator provides the results.

As an illustration of the experimental results where a cement sample was used, the following data were obtained:

$m_b = 47.2718$  [g] (cement mass)

$V_p = 17.2958$  [cm<sup>3</sup>] (true volume by pycnometer)

$\rho = 2.733$  [g/cm<sup>3</sup>] (true density by pycnometer)

$A_b = 7.045$  [cm<sup>2</sup>] (diameter of bed) = 2.995 cm

$h = 4.26$  [cm] (height of bed)

$V_b = 29.817$  [cm<sup>3</sup>] (volume of bed)

$\epsilon = 0.4199$

$P = 142.68$  [kPa] (set pressure)  
 $P_o = 102.20$  [kPa] (atmospheric pressure)  
 $F = 271.99$  [cm<sup>3</sup>/min]  
 $\mu = 1.832E-5$  [Pa·s] (air, at 24 C)

The above data resulted in the specific surface area,  $S_a = 3797$  [cm<sup>2</sup>/g] (379.7 [m<sup>2</sup>/kg]).  
The radius of a capillary  $R = 1.4E-4$  [cm] (1.4E-6 m or 1.4  $\mu$ m).  
Number of capillaries  $N = 47.7E+6$

The permeability specific surface area is within range of reported specifications for various cements. The above model also provides the representative (equivalent) radius of a capillary and their number. Due to often used tortuosity factor, the length of a more realistic capillary should be longer than the height of the bed. But to avoid any speculative value of a tortuosity factor, or for that matter any geometrical shape factors, any such value can be considered as equal to one.

It is an over-simplification to describe a complex reality of porous particles of various sizes using such a general approach, but often a single number is used to give an idea about a complex quantity, e.g. like a value of mean or other from a particle size distribution data, perhaps for comparison only among similar materials. If the capillary diameter number can be considered as a representative pore size in the cement sample, then the diameter of 2.8  $\mu$ m can be classified as being in the macropore region. It can be safely assumed that such hypothetical capillaries are uniformly distributed. From the model of hexagonal (densest) packing of small circles within a larger circle (coverage of  $\pi/(12)^{1/2}$ ) and assuming equidistant capillary arrangement, the number  $N$  of such capillaries in the bed area would have radius of about 2  $\mu$ m. Therefore the distance between the capillaries in the bed is about 4  $\mu$ m. So from mathematical calculations only, it can be said, that there are  $N$  equivalent capillaries participating in the flow, each of radius 1.4  $\mu$ m, and separated from its nearest neighbors by 4  $\mu$ m (center to center).

It should be clearly understood, that such characterization parameter like surface area is only a theoretically calculated number that is highly dependent on a particular model used. The specific surface area obtained from permeability measurements is usually much lower than from BET technique, and it is a common agreement that the major contribution to surface area comes from smaller size pores and complex internal structure of pores, which are not accounted for in gas (air) flow techniques. However, in BET technique, the sample outgassing by using vacuum at high temperatures is one of the factors of obtaining high surface area. Very often the expected sample properties that are inferred from having such a large surface area are not reflected in real applications. Without such sample treatment the so-called BET surface area is smaller. The "active sites" that are available for adsorption at LN2 temperature of cleaned samples, are not necessarily available in real temperatures, atmospheres, or pressures used. The BET analysis uses only a very small amount of sample, but in actual applications where much larger amount of sample is used, only some portion of the high surface area can be effective due the transport phenomena in bulk volumes. The accepted parameter value, namely the N<sub>2</sub> molecule cross section (or other adsorbents), is also one of the weak points of BET method.

Relatively simple equipment is needed to accomplish gas (air) permeability measurements. A particular selection of pressure set point for measurements is not critical, as long as the reference pressure can be maintained constant. The same surface areas are expected, when setting a small pressure differences and obtaining small flow rate, or when setting a larger pressure differences and obtaining larger flow rates. Therefore, packed beds of diverse materials with various levels of permeability can be measured using the same permeability cell. The described absolute method for determination of the specific surface area should be used with instruments operating under constant pressure above the bed and accurately measuring the resulting gas (air) flow rate.

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