

**NOTES TO THE EVALUATION OF GAS PERMEABILITY OF CONCRETE**  
- A Reply to the Discussion by F. Jacobs

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First of all, I would like to express my sincere thanks to Dr. Jacobs for the comments on my paper. And I am very much appreciated to the rearrangement of some of my data and the empirical analysis, i.e. plotting  $k$  vs  $1/P_m$ , by Dr. Jacobs.

I would like to take this liberty to point out, however, that (i) the deviation of the  $k$  from the linear relation to  $1/P_m$  at low  $P_m$ , which is shown in the discussion, is not due to the experimental error, namely the non-steady state (I tested each point by both increasing from lower pressure and decreasing from higher pressure, besides the time of waiting was long enough) and the accuracy in reading the flow rate; and (ii) the explanation proposed by Klinkenberg for the higher  $k$  determined at low  $P_m$ , i.e. the gas slip at the wall results in an additional flow, is in fact not adequate.

In the following, I would like to dwell theoretically upon (1) the time needed for establishing steady state flow, and (2) the mechanism of gas flow in micro-meso-porous material, which leads to the linear relationship between  $k$  and  $1/P_m$ , to discuss with Dr. Jacobs. The data presented here are obtained from another experimental work (using pure  $N_2$  and pure  $O_2$ ), for which the pressure was monitored by a pressure transducer (reading accuracy about 0.02 kPa) and the gas was finely regulated so that during each testing the pressure variation was less than 0.2 kPa.

### 1. Time Needed for Approaching the State of Steady Flow

Let us begin with the flow mechanism, i.e. the mass conservation law (or *continuity equation*) for one dimensional flow:

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} = 0 \quad (1)$$

where  $\rho$  is the density and  $u$  the rate of mass flow across a unit area. Applying the Darcy's law (on a material with porosity  $\epsilon$ ) for  $u$  and ideal gas law for the density, one obtains:

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x} \left[ -\frac{k}{\epsilon \mu} P \frac{dp}{dx} \right] = 0 \quad (2)$$

with initial condition  $p(x,0) = P_1$ ; and boundary conditions  $p(0,t) = P_2$ , and  $p(l,t) = P_1$ . In analogy to the diffusion equation:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x} \left[ -D \frac{dC}{dx} \right] = 0 \quad (3)$$

with initial condition  $C(x, 0) = 0$ ; and boundary conditions  $C(0, t) = C_1$ , and  $C(l, t) = 0$ , the permeability is equivalent to a Fickian diffusivity given by

$$D = \frac{k}{\epsilon \mu} P \approx \frac{k}{\epsilon \mu} P_m \quad (4)$$

where  $P_m = (P_1 + P_2)/2$ . Hence, mathematical solutions to the diffusion problem can be used to estimate the time needed for establishing the steady flow state. Although so calculated diffusivity varies with pressure, it is obvious that the error induced will be small if the pressure gradient is small. Under a constant gradient, the flow going through a large plane sheet is

$$Q(t) = \frac{DC_1A\epsilon}{l} \left[ t - \frac{l^2}{6D} - \frac{2l^2}{\pi^2D} \sum_1^{\infty} \frac{(-1)^n}{n^2} \exp(-Dn^2\pi^2t/l^2) \right] \quad (5)$$

at  $t \rightarrow \infty$ , the exponential term  $\rightarrow 0$ , and  $Q(t)$  approaches the line which has an intercept  $t_0$  (time-lag) on the t-axis [1]:

$$t_0 = \frac{l^2}{6D} \quad (6)$$

This clearly shows the dependance of time needed for establishing the steady flow state upon permeability and pressure. In my experimental work, it is observed that the steady state is assumed at about  $3t_0$  (Fig. 1), in agreement with that  $2.7t_0$  (i.e.  $Dt_0/l^2 = 0.45$ ) stated by Crank [1]. Likewise, the time of waiting can be checked out by  $t \geq \epsilon\mu l^2/(2kP_m)$ . It should be pointed out that the time-lag method measuring the diffusivity indicating **how fast** the gas moves (in dry sample where dissolution of gas in pore water is negligible), is also a well known method [1, 2]. Combining eq(4) with eq(6) results in that the open pore porosity can be estimated by

$$\epsilon = \frac{6 t_0 k P_m}{\mu l^2} \quad (7)$$

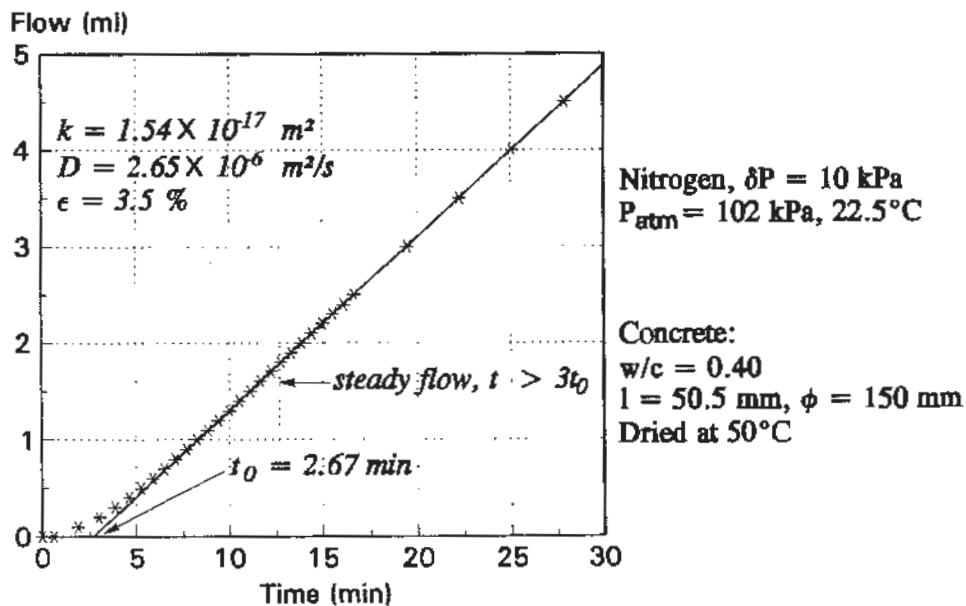


Figure 1 Approaching to steady-state flow through a concrete specimen.

## 2. Gas Flow in Micro-porous Media

Why the  $k$  vs.  $1/P_m$  plot reveals a straight line over a moderate high pressure range? Klinkenberg found this phenomenon and did a great job to confirm this trend, which was an important contribution to the understanding of the mechanisms of gas flow through micro-meso-porous material. It is known that Klinkenberg derived an formula to relate the liquid and gas permeability:

$$k_l = \frac{k_g}{1 + \frac{b}{P_m}} \quad (8)$$

on an assumption that at higher pressure, gas is approaching to liquid. Bamforth [4] tested the intrinsic permeability (in  $\text{m}^2$ ) liquid and gas through concretes, and largely confirmed this formula; and proposed that gas permeability should be performed at a mean pressure higher than 1 MPa. It should be noted that, however, in the case of testing concrete permeability by conventional method, the side at normal pressure can never reach to a high pressure thus the gas there can never become a liquid, and the assumption by Klinkenberg is somewhat incorrect.

Nevertheless, it was very correctly pointed out by Klinkenberg, as stated by Dr. Jacobs, that this phenomenon (linear  $k$  vs.  $1/P_m$ ) was due to the influence of pore size, i.e. when the pore size is comparable with the free-path of molecules, the behavior of gas flow is different.

The mechanisms behind are: (a) the higher  $k$  exhibited at lower  $P_m$  may be due to an additional flow resulted from the gas slipping at the wall, as mentioned by Dr. Jacobs; (b) the flow of gas in such small pores is dominated by Knudsen flow [2], which is proportional to the pressure gradient, thus the formula used for evaluating  $k$  (see the original paper) results in a permeability coefficient varying by a factor of  $1/P_m$ . Let us analyze them one by one.

### 2.1 Increase of apparent viscosity of gas due to gas slipping at the wall

It is equivalent to say that slipping gas increases the viscosity as that adds more flow. The theoretical treatment of this problem is well established (see, e.g., Chapman and Cowling [3]). It needs only to cite the result, that due to the slipping at the wall, the apparent viscosity becomes

$$\mu' = \frac{\mu}{1 + 2n \frac{l_0}{r} \frac{2-\Theta}{\Theta}} \quad (9)$$

where  $l_0 = (1/(2^{1/2}\sigma))k_B T/p$ , is the mean free path of molecules,  $\sigma$  is the collision area,  $r$  is the radius of the pore,  $n$  is a numerical factor of order unity (defined as: the distance between moving flow and wall is  $nl_0$ ) and  $\Theta$  is the fraction of molecules striking the wall and then enter the flow. This effect is more pronounced in small pores when  $l_0$  and  $r$  are comparable. But, it must be noted that this treatment fails when  $l_0$  exceeds  $r$  [3].

Recall the formula by Klinkenberg (eq 8), one can derive that  $b = 2nk_B T(2-\Theta)/(\Theta\sigma\sqrt{2})$ , and apparently the linear relationship between  $k$  and  $1/P_m$  can be established. Bamforth [4]

obtained  $b = 0.1$  to  $1000$  for concrete, or  $b = 1.635 \times 10^{-8} k^{-0.5227}$  ( $P_m$  in atm,  $k$  in  $m^2$ ). For example, if  $k = 3 \times 10^{-18} m^2$ , then  $b = 24$ . This, in term of reduction in viscosity, is about 25 times at  $P_m = 1$  atm, a value far too high.

On the other hand, considering that as Dr. Jacobs stated, the reason is the speed of molecules at wall surface is not zero which thus adds to the speed, one still cannot get a satisfactory answer. It may be recalled for that in derivation of Poiseuille equation or eq(1) in my original paper by continuity equation, the size of the pore is assumed to be large enough to accommodate enough molecules, so that it makes no difference if the zero speed is referred to the wall or to the adsorbed molecules on the wall. Furthermore, this, if it is true, leads to an additional flow volume not more than one molecule layer at the wall, which in large pore is not important. Therefore, the gas slipping effect is not the main reason for the linear  $k$  vs  $1/P_m$ .

## 2.2 Gas flow in concrete is partly governed by Knudsen diffusion

In a small pore, where  $r$  is comparable or less than  $l_0$ , the collision between molecules is comparable with or even less than that with the wall, a molecule hitting the wall will exchange energy with the wall, thus it bears no relation to the velocity of the incident molecule, and its direction is purely random [2]. This means that the collision with the wall *adds no extra flow* in very small pores. The transport process in this regime is known as **Knudsen diffusion**, and the mechanism predicts that, in a cylindrical pore, the velocity of molecule is

$$u = -\frac{D_k}{ck_B T} \frac{\partial p}{\partial x} ; \text{ where } D_k = r \sqrt{\frac{32}{9\pi} \frac{k_B T}{m}} \quad (10)$$

where  $c$  is the concentration,  $k_B$  Boltzmann constant,  $D_k$  Knudsen diffusion coefficient, and  $m$  the molecule's mass; derived by the force balance between pressure over the pore cross section and the momentum flux to an element of the wall. Substituting this (and applying ideal gas law for  $c$ ) into the continuity equation, one obtains

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x} \left[ -D_k \frac{dp}{dx} \right] = 0 \quad (2-a)$$

In the pores of size in transition regime, both the Poiseuille mechanism and Knudsen mechanism are functioning, and the effects are addable, thus

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x} \left[ -\left( \frac{k}{\epsilon \mu} p + D_k \right) \frac{dp}{dx} \right] = 0 \quad (2-b)$$

At the steady state, the flow rate of gas is

$$\frac{Q}{A} = \frac{k}{\mu} \frac{P_2^2 - P_1^2}{2lP_1} + \epsilon D_k \frac{P_2 - P_1}{lP_1} = \left[ \frac{k}{\mu} + \frac{\epsilon D_k}{P_m} \right] \frac{P_2^2 - P_1^2}{2lP_1} \quad (11)$$

It can be calculated that the mean free paths of  $N_2$  at 293 K are 66 nm and 19 nm for pressure 101 KPa and 350 KPa respectively; and the corresponding values for  $O_2$  are 71 and 20 nm. The pore size of cement paste includes this range, i.e. from nm to  $\mu m$  [5]. Thus the Knudsen flow is dominating at normal pressure for gas transport in concrete. It is pertinent to

compare the magnitude of Poiseuille flow with that of Knudsen flow in a cylindrical tube, as is shown by Kärger and Ruthven [2], to see that in small pores or at low pressure, Poiseuille flow is much weaker than Knudsen flow, Table 1.

Table 1 Relative importance of Knudsen Diffusion and Poiseuille Flow for Air at 20°C in a Straight Cylindrical Pore (after Kärger and Ruthven [2]), where  $D_{\text{Poiseuille}} = pr^2/(8\mu)$ .

p (atm)	r (m)	$D_k$ ( $\text{m}^2/\text{s}$ )	$D_{\text{Poiseuille}}$ ( $\text{m}^2/\text{s}$ )	$D_{\text{Poiseuille}}/(D_k + D_{\text{Poiseuille}})$
1.0	$10^{-8}$	$3 \times 10^{-6}$	$7 \times 10^{-8}$	0.02
	$10^{-7}$	$3 \times 10^{-5}$	$7 \times 10^{-6}$	0.19
	$10^{-6}$	$3 \times 10^{-4}$	$7 \times 10^{-4}$	0.70
10	$10^{-8}$	$3 \times 10^{-6}$	$7 \times 10^{-7}$	0.19
	$10^{-7}$	$3 \times 10^{-5}$	$7 \times 10^{-5}$	0.70
	$10^{-6}$	$3 \times 10^{-4}$	$7 \times 10^{-3}$	0.96

Figure 2a shows rates of  $\text{N}_2$  and  $\text{O}_2$  flowing through concrete under different pressure differences, and Figure 2b shows the  $k$  vs.  $1/P_m$  plot of these data. In Figure 2b, a straight line at moderate pressure range is in full agreement with the theory, while the deviation at low pressure ( $P_m < 50$  KPa) range is due to the fact that Knudsen diffusion dominates. The latter can be seen, very obviously, when plotting the flow against the pressure difference (Fig.2a), which reveals that at low pressure, the flow rate is proportional to the pressure gradient. Comparing  $\text{N}_2$  flow with  $\text{O}_2$  flow, the ratio of the slope of  $Q(t)$  vs.  $\delta p$  plot which is proportional to  $D_k$ , gives  $D_{k, \text{Nitrogen}} : D_{k, \text{Oxygen}} = 1.07$ , and the ratio of slopes in  $k$  vs.  $1/P_m$  plot after correction for viscosity gives  $D_{k, \text{Nitrogen}} : D_{k, \text{Oxygen}} = 1.05$  (c.f. the data in Figure 2b). This is to be compared to the theoretical value  $\sqrt{(32/28)} = 1.069$ , whereas the ratio of the viscosities of the two gasses is 1.16. It is seen that the  $D_k$  obtained by  $k$  vs.  $1/P_m$  (Fig.2b) is about 80% of that obtained according to a complete Knudsen diffusion mechanism, which probably indicates the flow is in pores of an average size  $r = 1000 \text{ \AA}$  (Table 1).

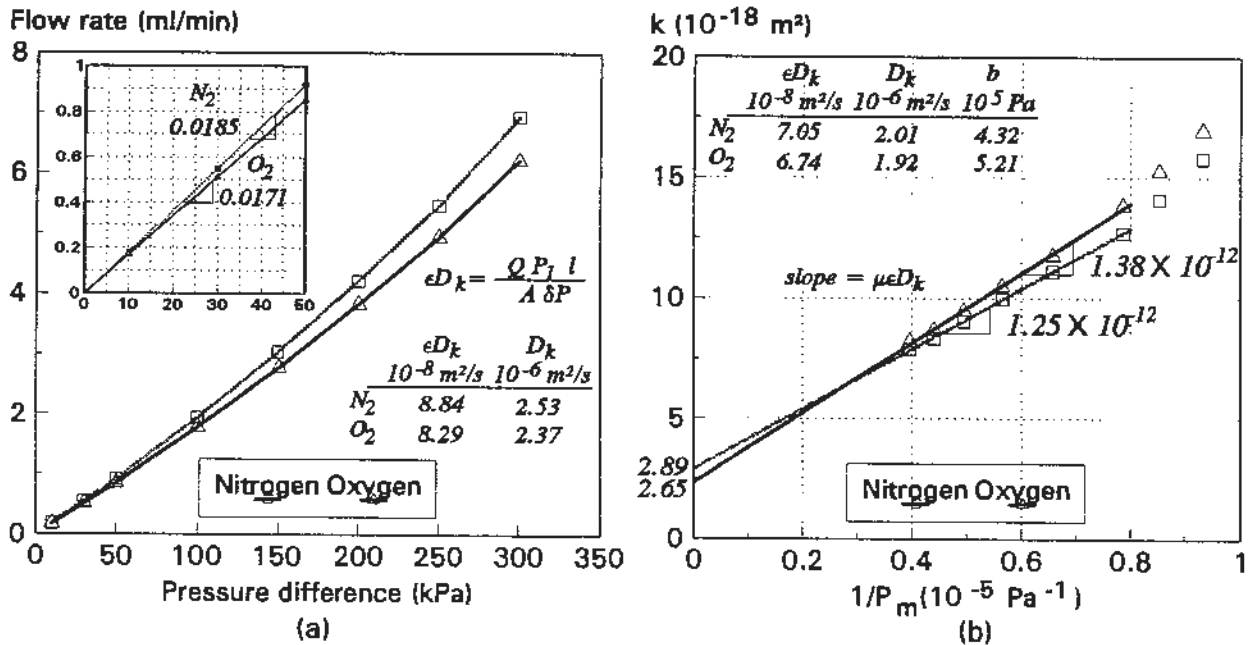


Figure 2 Flow rate and permeability as functions of pressure, (the same specimen as in Fig.1).

### 2.3 $b$ value in Klinkenberg equation

Equation 12 leads to that the permeability coefficient evaluated according to Poiseuille flow-only mechanism

$$k' = k + \epsilon \mu \frac{D_k}{P_m} = k \left( 1 + \frac{\mu}{k} \epsilon \frac{D_k}{P_m} \right) \quad (12)$$

Comparing with the Klinkenberg's equation ( eq 8 ), it is obvious that its empirical coefficient  $b = \mu \epsilon D_k / k$ . The data shown in Figure 2b result in  $b = 4.3 \times 10^5$  ( $P_m$  in Pa). This indeed gives a right order of magnitude compared with the experimental data by Bamforth [4]. This also clearly reveals that the value of  $b$  increases with porosity and  $D_k$  (note:  $D_k$  also increases with porosity for it reduces the tortuosity of flow path, as I mentioned in my original paper), and with the decrease in  $k$ . It should be mentioned that  $b$  value obtained in this work is about 5-fold smaller than that shown by Bamforth [4] who compared the gas permeability with the water permeability. The lower water permeability may be due to the influence of the long-range molecular force by the wall on the liquid in pores, which however is beyond the scope of this reply paper.

According to the above discussion, it can be summarized that the gas flow in concrete is governed by Knudsen diffusion and Poiseuille flow mechanisms. The intrinsic permeability  $k$  (at  $1/P = 0$ ) and the constant  $b$  obtained by  $k$  vs.  $1/P_m$  plot indicate the transport properties of concretes, namely permeability, open-pore porosity and Knudsen diffusion coefficient (which depends on the type of gas). On the other hand, the gas slipping effect is of only a minor importance.

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