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Proposal of quadratic equation for prediction of flow rates versus pressure in packed beds of cement

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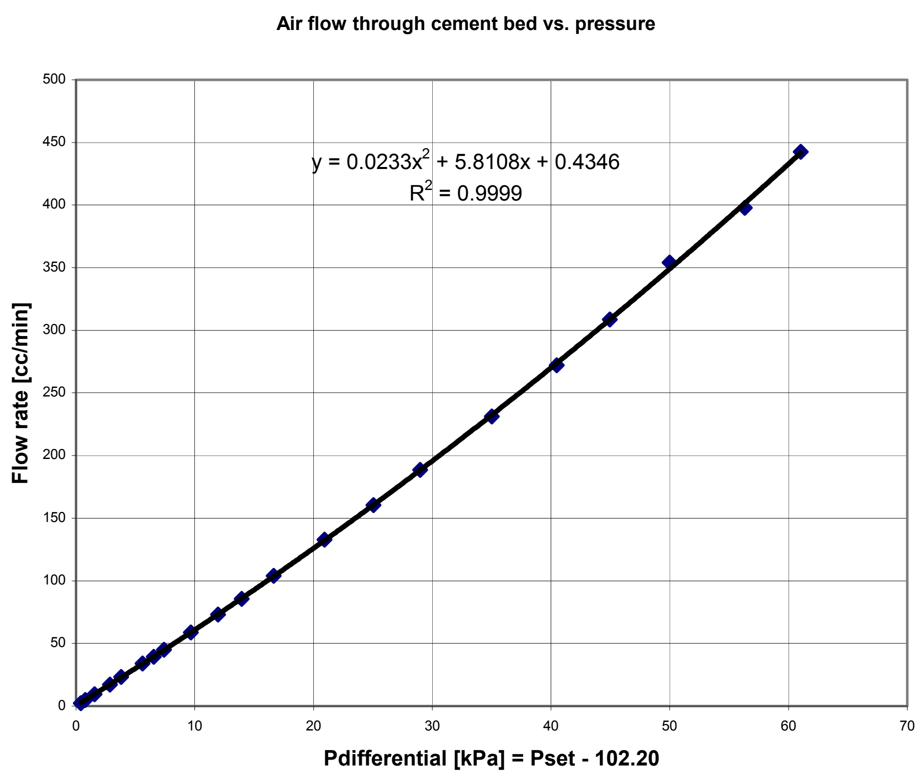
Based on experimental measurements of flow rates versus pressure in a packed bed of cement, the quadratic relationship is obtained and discussed. The coefficient at quadratic term is proposed as the basic parameter for characterization and extraction of other parameters of interest. Advantages of the equipment over Blaine apparatus used in ASTM C 204 method are presented.

A versatile cell for studying flow resistance in packed beds, cement beds in particular, was devised and combined with the PV-Pyc 200 gas pycnometer hardware and software. The main purpose was to obtain data for evaluation of powder (cement) properties, but without the restrictions, like a certain value of bed porosity, that many simplified methods use in cement characterization. The photo below shows a particular setup for measurement of flow rates, where gas is supplied to the top of the cell using the precision pressure regulator of the pycnometer to set appropriate pressure values and measure the resulting flow amounts from the bottom of the cell. For many practical reasons, the output flow from the bottom of the cell was measured by a bubble flow meter of 50 cc capacity and a digital timer (stop-watch).

The PV-Pyc 200 can be equipped with dual gas option, so the user can carry out flow measurements using two different gases with the convenience of selecting one of them by using the front panel switch. Using the Manual Mode in the software, the pressure values set by the pressure regulator are measured by the pressure transducer of the pycnometer. Knowing these absolute pressure values, and previously determined value of the atmospheric pressure, the differential pressure values corresponding to each flow rate can be obtained. Therefore, the need of having a differential pressure transducer across the cell is eliminated, but one can be installed if desired.

From experimental point of view it is convenient to keep one side of the packed bed at the atmospheric pressure (or vacuum) as the reference and apply a certain flow or set pressure at the other side of the bed. In the presented example, the various pressure values were set at the top of the bed as an independent variable and the bottom of the cell was kept at atmospheric pressure. It is tacitly assumed, that gas source is infinite and for the rather small amounts of the gas used in this case, the pressure regulator is able to provide it. The pressure difference between the top and bottom of the packed bed is the driving force and the resulting flow of gas (air) is the response. The pressure difference is the independent variable (abscissa) and the flow rate is the response (ordinate) in this case. In many other applications, especially in fluidized beds, the known flow is applied from the bottom and the resulting pressure difference is measured.

The mass of 47.2718 g of cement sample was weighed and the true volume of 17.296 cm^3 (true density of 2.733 g/cm^3) was obtained by using the PV-Pyc 200 pycnometer. Semi-dry air (dew point about -5 C) was used as the carrier gas. A packed bed of diameter close to 30 mm and height of 42.6 mm was prepared and a vibrator was used to obtain the best possible packing. The calculated geometrical volume from the measured bed dimensions is 29.817 cm^3. The void volume is defined the difference between the physical volume and the true volume, and when divided by the physical volume it yields the porosity, ε, of the bed. In this case the porosity value of 0.4199 was obtained.



The chart above shows the results of flow rates measurements through the above-described cement bed. A fitted trend line through the data points exhibits good correlation with a quadratic equation. This is a bit different result then expected as numerous literature examples utilize Carman-Kozeny equation for the laminar flow region, which for a fixed bed predicts linear relationship between flow rate and pressure drop.

In the PV-Pyc 200, there is also a possibility of utilizing the embedded miniature vacuum pump to obtain a certain vacuum level as the reference instead of atmospheric pressure by connecting the vacuum pump to the bottom of the cell. A fairly constant vacuum level of 7.13 kPa can be maintained at low flow rates. The top of the cell was equipped with a precision metering valve that allows for increase of the pressure values from that vacuum level to some higher values. The photo below shows partial hardware arrangement for measuring airflow rates using such a vacuum reference. The pycnometer has to have a bit different internal construction then the standard version to implement this capability. Any other suitable (diaphragm) vacuum pump can be used and either a differential pressure transducer across the cell or another absolute pressure transducer at the bottom of the cell can be utilized for improved setups.

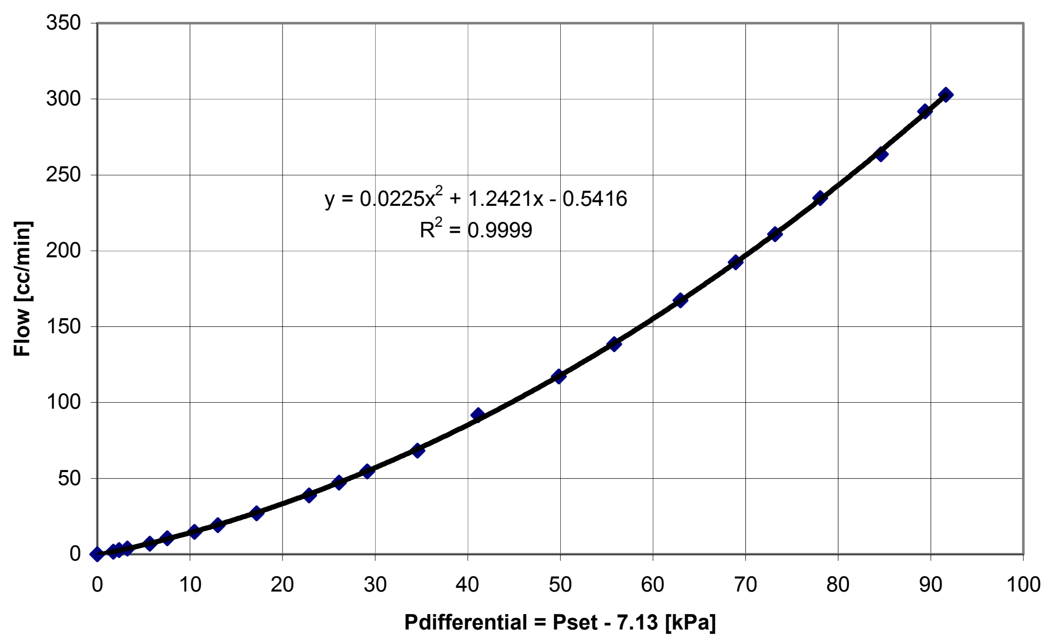
The gas (air) flow is measured from the vacuum pump output. In order to make such flow measurements possible from the vacuum pump output and eliminate flow noise, a special muffler has been designed and placed between the pump output and the bubble meter input. Although there were some concepts published in literature in the past using glass apparatuses, and even commercial products utilizing so-called Knudsen region were offered, this design is far more advanced and offers direct flow measurements.

With the valve which supplies gas to the pycnometer being closed, the pressure transducer is being used for measurements of the pressures at the top of the cell. The extra hardware added to the top port of the external cell consists of precision metering valve and filter. When the metering valve is closed, the pressure above the bed gets reduced to the vacuum level produced by the pump and no flow through bubble meter can be detected. From that vacuum reference, the metering valve can be slightly opened to allow some flow and a certain pressure level buildup. Obtaining flow values at established various pressures (up to the atmospheric pressure in this setup) above the lowest vacuum level, the curve of flow rates versus pressure differentials can be obtained.

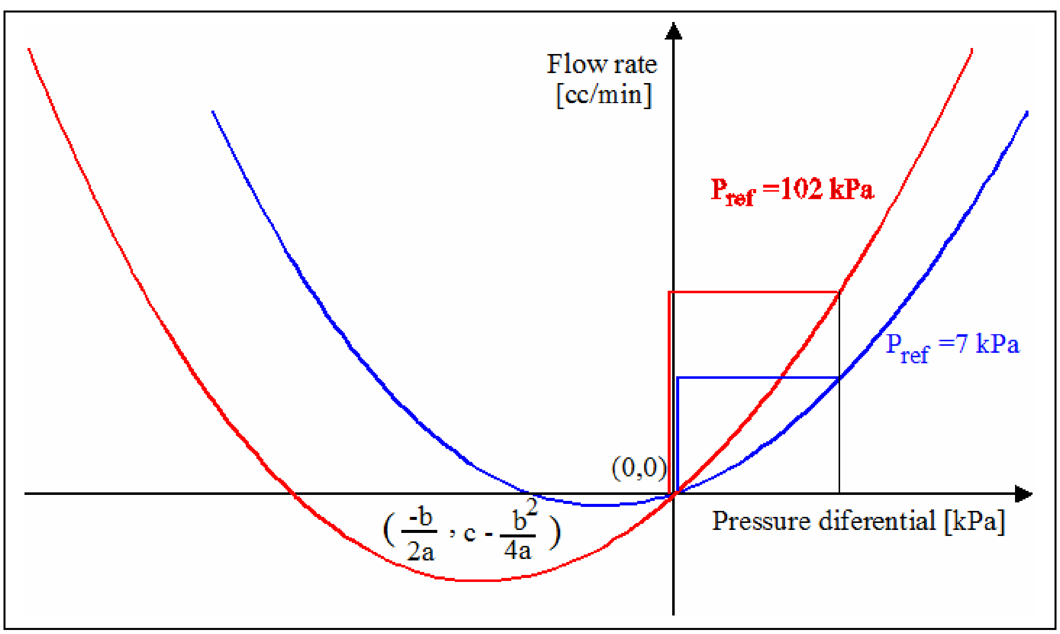
The main reason for using either atmospheric pressure or some low vacuum level for obtaining flow data versus pressure differential was to find out if indeed any different flow characteristics can be obtained for finely packed powders and if any desired properties can be deduced. It is possible to use as a pressure reference a pressure value set well above the atmospheric pressure, but more complicated hardware setup is required, and it is doubtful to be more productive.

The graph below shows the flow rate curve where the bottom of the cell was maintained initially at 7.13 kPa although most likely it has slightly increased with flow rate due to limited pumping capacity of the pump. The same unaltered bed with cement was used. Again, the data points are strongly correlated to a quadratic function when plotted as obtained, the flow rate values versus the set pressure differentials. It is interesting to see, that the coefficients at the quadratic terms seems to be very similar for the two different flow regions, while the coefficients at the linear term are far more different, although the one at the vacuum reference is smaller then the one at atmospheric pressure reference

Air flow through cement bed vs. pressure



Further analysis suggests, that this can be actually the same parabola but with vertex location dependent on the selection of the reference pressure level. This can be seen more clearly when both fitted trend lines are presented on the same graph.



The above graph is not to scale and it is presented for illustration only. The formula for calculations of the location of vertexes is also provided. Both parabolas cross the origin of the coordinates as the flow rates start increasing from zero when the pressure differential also increases from zero to positive values. If a low enough pressure is used as a reference, then the curvature of the parabola is more pronounced and it is harder to be ignored. When using a higher-pressure reference, like the convenient atmospheric pressure, the steeper part of the parabola is involved, and using only a small range of measurements and/or not high enough accuracy, often a linear relationship is claimed.

It is easy to notice that both parabolas must have two roots, one at zero (as we start collecting data there), and one on the negative side of the abscissa (as the pressure reference is practically always greater then zero vacuum). Mathematically, if the quadratic equation in general form $y = ax^2 + bx + c$, is stipulated to have one root equal to zero, then necessarily the coefficient c must be zero, and the second root value is equal to -b/a. Therefore, the equation relating flow rate with pressure differential can be written as:

$$\textbf{Flow rate [Volume/time]} = \mathbf{a \cdot \Delta P \cdot (\Delta P + b/a)} \qquad \textbf{(Eq. 1)}$$

where the a and b are constants and the ΔP is the pressure differential, $P - P_{ref}$. After carrying out the multiplication, the simplified equation has the form:

$$\textbf{Flow rate [Volume/time]} = \mathbf{a \cdot \Delta P^2 + b \cdot \Delta P} \qquad \textbf{(Eq. 2)}$$

It has been a well known experimental fact and often reported in literature, that pressure differential, ΔP across a packed bed was better described by using a quadratic relationship,

$$\Delta P = \alpha \cdot u + \beta \cdot u^2, \qquad \text{(Eq. 3)}$$

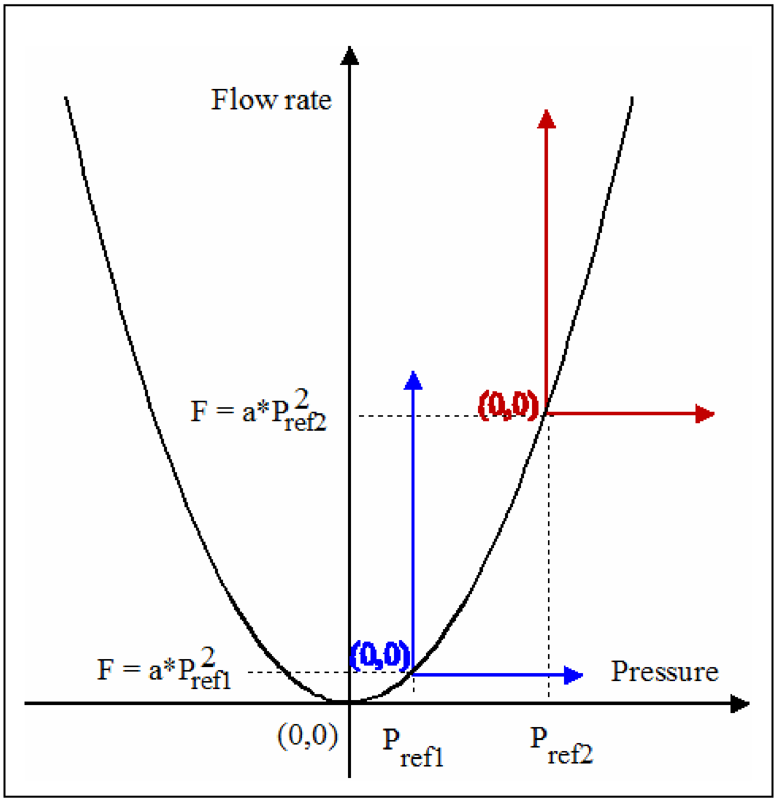
then just by a linear one (e.g. Darcy model). The α and β are constants, and u is (related to) flow rate. There have been many attempts to come up with a useful practical solution resembling this relationship. In this case the u is independent variable and the ΔP is the response. Practically all equations of that sort are based on many (geometrical and experimental) assumptions, which can be hard to justify but perhaps necessary to produce some form of analytical expression. With enough of "fudge factors" is it possible to arrive at a reasonable agreement with experiments.

If the two parabolas have similar coefficient a, and the coefficient c is equal to zero (or close to it), the coefficient b at the linear term is rather related to the shifting of the parabola due to particular selection of the pressure reference P_{ref}. Therefore, it does not carry any additional information then the coefficient a at the quadratic term, as the P_{ref} is usually known. Therefore, any attempts to figure out any characterization properties should be concentrated on working with the coefficient a (or β in Eq. 3).

The parabolas can be "unified" by shifting their vertexes to the origin of the coordinate system. The graph presented below shows a single parabola but with the local or experimental coordinate systems pertinent to selection of P_{ref} shifted to the right and up. The marked values on the ordinate show the flow rates that would be obtained if the particular pressures of the values of the positive references were used, and referenced relative to the absolute vacuum. The flow rate equation can be expressed in this following representation as dependent only on the pressure and the coefficient a.

$$\textbf{Flow rate [Volume/time]} = \mathbf{a \cdot P^2 - a \cdot P_{ref}^2} \qquad \textbf{(Eq. 4)}$$

Mathematically the vertex can be located at (0, 0) when the $P_{ref} = 0$ is used. Since the zero vacuum is practically not attainable, especially if a non-zero pressure is applied and continuous flow results, the vertex is always shifted somewhat away from the origin of (0, 0). The small values of the constant c, ($y = ax^2 + bx + c$), that is obtained from fitting experimental data to quadratic equations, is a result of non-ideal maintaining of the fixed pressure reference and presence of some amount of experimental errors. Experimentally, the coefficients a are also not expected to be ideally the same at different P_{ref}.



In packed beds consisting of coarse material with large interstitial spaces, where gases can travel without much restriction, and at relatively low flow rates, a linear relationship between flow rates and pressure differential is adequate. In cases of fine powders like many cementitous materials, with substantial porosity and large range of particle size distribution, and with particles being of highly complex shapes and structure, the interstitial passages get substantially reduced in a well-packed bed, and porosity of the powder can play a relevant role in gas transfer through such beds. The linear relationship between the flow rate and pressure is no longer valid and a more complex equation, e.g. in quadratic form, is needed. To describe a continuum of cases when passing from linear to non-linear relationships, it is tempting to use a variable exponent instead of the fixed value of 2 in the equation 4. However, this causes a problem related to physical meaning of the quantities, as the units cannot be reconciled.

Once the experimental results of measuring flow rates versus pressure are obtained, it is expected to obtain more information about the substance used. Presenting simple and producing good results method is highly important. It seems that utilizing popular Carman-Kozeny or similar models to extract specific surface area is the next step. It should be kept in mind that all the models are crude and do not produce great results as they try to describe such a complex reality by simple geometrical considerations.

Obtaining reliable (absolute) values of the highly sought surface area parameter is rather unlikely by any method known. Since the values depend on the method used, and any particular model employed, the often-reported in literature is a specific surface area. A compromise in such situation is to use a comparative approach. First, for a given class of materials tested, the relationship between the flow rate and pressures needs to be established by measuring a series of flow rates versus pressure levels. Once the functional dependence is found, then it is enough to make just one determination of flow rate at a selected pressure set point. Such a relationship can be useful to see if usage of different gases, (lower) temperatures, or other factors has any impact on it. For very simplistic approaches, knowing such functional dependence is not all that necessary. To avoid any additional complications, the same procedure of the packed bed preparation should be used. It is recommended to use the same height of the bed. Weighing a larger amount of sample then needed, and reweighing the unused portion after using a sufficient amount to arrive at the same bed height, is a simple way to achieve the same bed height. Although incorporation of packed bed geometry is practiced by dividing/multiplying by surface area and bed height, it is not that certain that linear correction of bed height is the proper way for non-linear relationships between flow rates versus pressure.

For comparative approach it is important to select the reference material, which should be representative for the studied samples. Many aspects like, available characterization by other methods, general acceptance, reproducibility, availability, invariance with time, etc. will need to be considered. Or it can be just the master material before adding any additives or carrying out any thermal or other treatment of the material.

The simplest comparison among sample can be done by comparing the value of the coefficient a (Eq. 4)

$$\mathbf{a = Flow\ rate / (P^2 - P_{ref}^2) \qquad (Eq.\ 5)}$$

In permeability models, the quantity similar to the coefficient a is rather a complex set of other parameters, like density, porosity, dynamic viscosity of gas, bed geometry, specific surface are, etc. The specific surface area is squared and in the denominator part in equations of flow versus pressure. So, following such formulas, two values of coefficient a are obtained for the reference material (REF) and for the sample (SAM): $\mathbf{a_{REF} = Constant/S_{REF}^2}$, $\mathbf{a_{SAM} = Constant/S_{SAM}^2}$, where S_{REF} and S_{SAM} stand for specific surface area of reference and sample, respectively. The specific surface area of sample can be easily evaluated as

$$\mathbf{S_{SAM} = S_{REF} \cdot \sqrt{(a_{REF} / a_{SAM})} \qquad (Eq.\ 6)}$$

If the S_{REF} is not known, then the value of 1 can be substituted for S_{REF} , and the simplified square root of coefficients ratio can be employed to estimate the sample area relative to the reference material used.

If in any experimental setup a fixed and repeatable value of pressure P is ensured, and the reference pressure, which is typically atmospheric and is relatively stable for a given period of carrying out the experiments, the flow rates for the reference material and the sample can be compared. If using a bubble soap meter where the bubble travel the burette between fixed marks, only the time measured can be utilized. Denoting the time for reference and sample as t_{REF} and t_{SAM} , respectively, the simplest formula can be utilized:

$$\mathbf{S_{SAM} = S_{REF} \cdot \sqrt{(t_{SAM} / t_{REF})} \qquad (Eq.\ 7)}$$

One can easily notice, that such relationship is used in the standard method ASTM C 204-07 for determination of fineness of hydraulic cement by Blain air-permeability apparatus. More complex equations based on Carman-Kozeny equation are presented in this ASTM method which sequentially incorporates additional information, like viscosity, porosity, density, and a constant equal to 0.9 is specifically appropriate for hydraulic cement.

It should be clearly understood, that the specific surface areas obtained by highly simplified equations 6 or 7, could provide merely an experimental trend, not the absolute values. Despite of preservation of all the same experimental conditions, most likely, some properties of the sample and reference material will differ, e.g. density or porosity. Therefore, more detailed treatment is necessary to account for variations of such properties in order to extract results that are believed to be related closer to the actual specific surface area.

The presented equipment consisting of PV-Pyc 200 and the external cell (with auxiliary hardware) offers several advantages over the Blain apparatus for characterization of cement samples:

1. The sample porosity is not restricted to about 0.5 values, as often it is not physically possible to achieve such packing for most samples. The uniformly packed bed can be achieved by using vibrations and holding the plunger with finger force, not just only by forcing the plunger down the cell. What is important to mention, is that porosity and density of materials can be conveniently measured using the pycnometer, which is not offered by the Blaine apparatus.

2. More representative sample size can be used for the packed bed preparation, e.g. 3 cm diameter, to over 4 cm in height. There are also ways of using different bed sizes as either different cells or adapters can be utilized.

3. The sample can be purged with air for some time before taking measurements at steady state flow conditions, not dynamic ones. Moreover, a dry or semi-dry air can be used, generally a gas of controlled dew point) and that removes any errors resulting of using ambient air with various humidity levels, as some constituents of the cement sample can be sensitive to it.

4. Other gases then air can be used in this setup while the Blain equipment uses ambient air.

5. There is no mercury involved or glassware, other then a separate bubble soap meter if one is being used for simplicity and accuracy.

6. The pycnometer setup allows for obtaining experimental data from which functional dependence between flow rates and pressure differential can be deduced. The capability of pressure regulation allows for selection of a suitable pressure setpoint to research materials having large range of permeability factor.

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