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A Smoking Gun Scenario Relative to Fluid Dynamics in Closed Conduits

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Abstract: Recent scientific articles published by many of the most popular authors in HPLC, based both in Academia, as well as at industry leading companies, regarding the relatively new technology in chromatography known as UHPLC, have increasingly focused on a methodology of evaluating the performance of packed chromatographic columns, by suggesting that the value of the Kozeny constant is variable, rather than a constant. This practice is totally invalid and, in addition, is demonstrably false. In this paper, we will prove, conclusively, that this is the case. In so doing, we will use the experimental data provided by these very authors themselves, in combination with well – settled fluid dynamics theory dating back to 1901, to prove that their conclusions relative to their calculated values for the Kozeny constant, are entirely without merit and not supported by their own measurements. In addition, we will further demonstrate that, based upon a newly minted theory of fluid dynamics in closed conduits, published for the first time in 2019, representing the most recently published reference in fluid dynamics, the unique constant value for this Kozeny parameter, which has been previously shown to be validated over the entire fluid flow regime, will be identified and applied to the reported data, thus, correcting for the errors made by the paper authors and ending approximately 150 years of ambiguity in the science of packed conduits and, HPLC, in particular.

Keywords: Forchheimer Coefficients, Specific Permeability, UHPLC, UPLC, Packed Beds

1. Introduction

We begin by introducing a methodology used in engineering circles, as opposed to chromatographic circles, called hydraulic gradient [1]. To put this term into context for all disciplines, we show the relationship between hydraulic gradient j and pressure gradient ($\Delta P/L$):

$$j = \frac{\Delta P}{\rho f g L} \tag{1}$$

Where ΔP = the pressure differential across the packed conduit and L = the length of the conduit.

We can see from the righthand side of equation (1) that hydraulic gradient, j, involves, not only, the pressure gradient, ($\Delta P/L$,) across a packed conduit, but also, includes the additional variables, ρ_f, the fluid density, and g, the acceleration due to gravity. Thus, from an empirical perspective regarding packed column permeability, a practitioner needs to identify the measured pressure drop, ΔP, at any given fluid flow rate, q, the length of the conduit, L, and, because both these following entities are already baked into the measured pressure drops, obtain from reference text books the values for the density of the fluid used in the measurement, ρ_f, as well as the acceleration due to gravity, g.

In addition, since it is customary when carrying out permeability determinations in packed conduits, to record the measured flow rate corresponding to the measured pressure drop, as fluid flux, μ_s, through the packed conduit, plotting fluid flux, μ_s, versus hydraulic gradient, j, is a popular engineering methodology. Thus, we can write:

$$\mu_s = \frac{4q}{\pi D^2} \tag{2}$$

Where, μ_s = fluid flux, also called linear superficial fluid velocity, q = volumetric fluid flow rate, D = the conduit diameter and π = a universal constant.

Accordingly, in order to use the fluid flux parameter, the practitioner must measure, in addition to the fluid volumetric flow rate, the conduit diameter, which means that, when evaluating the permeability of packed conduits experimentally, he must ascertain, independently, the values of D, L, q, ΔP, η, ρ_f, g and π, i.e., 8 independently determined entities.

Where, η = the fluid absolute viscosity.

2. Methods

The Forchheimer Fluid Flow Model

When reporting empirical results of permeability in packed conduits, the Forchheimer fluid flow model is a popular engineering methodology, especially when the fluid flow regime involves significant kinetic contributions [2]. We can write the Forchheimer equation as follows:

$$j = a\mu_s + b\mu_s 2 \tag{3}$$

Where, a, and b, are the Forchheimer coefficients for the viscous and kinetic contributions, respectively.

Thus, we can see from equation (3) that hydraulic gradient is a quadratic function of fluid flux. It is customary in engineering circles to make a plot of equation (3), a typical example of which is shown in Figure 1.

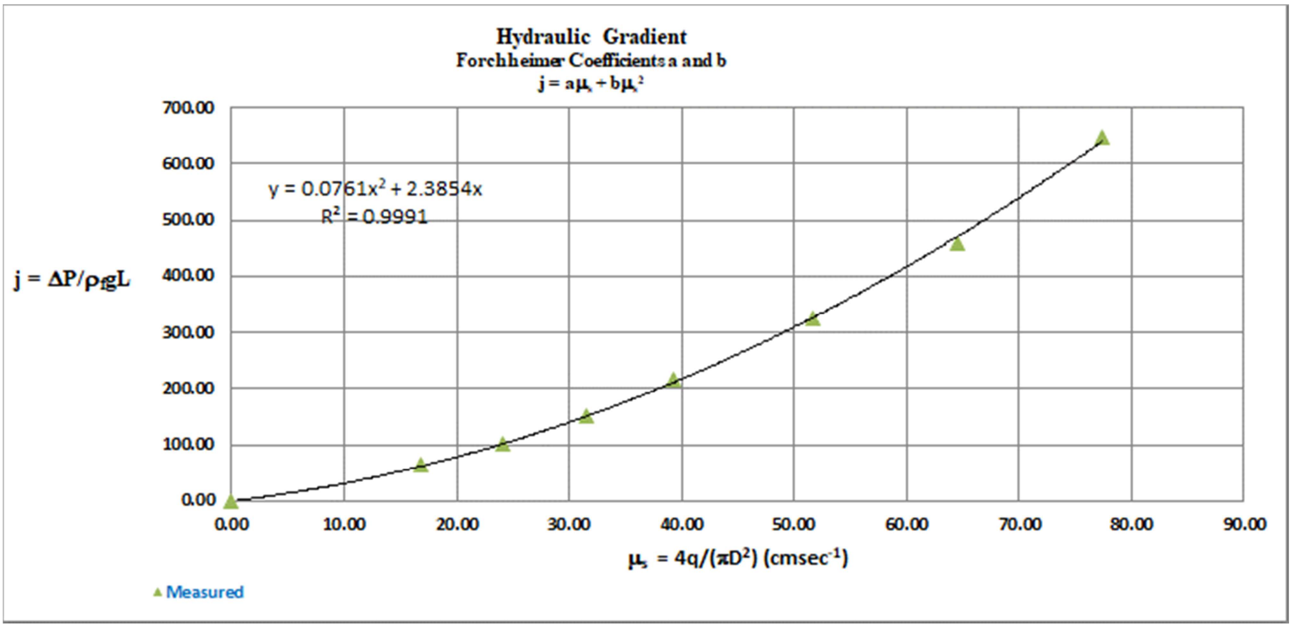

Figure 1. *Forchheimer coefficients.*

As shown in Figure 1, the second order polynomial trend line associated with this plot, which contains only measured values, renders the values of a, and b, both of which are represented as having a constant value, over all flow rate ranges, when there are no significant wall effects, i.e., at large values of the D/d_p ratio. Thus, we can describe the Forchheimer coefficients, a, and, b, as “residual fudge factors” which guarantee that, not only, does our measured values for pressure gradient correspond exactly to our calculated values, on the one hand, but also, on the other hand, the correct mix of viscous and kinetic contributions embodied in our measured values for pressure gradient will be maintained in our calculated values.

Darcy’s Law

When experimental measurements are confined to the flow regime known as laminar, which is typically the case in the chromatographic columns depicted in published articles relative to UHPLC, the value of the modified Reynolds number, R_{em}, is always less than unity and the plot in Figure 1, above, will appear linear, as opposed to curved. In this scenario of empirical data, Darcy’s Law is typically used to justify the pressure flow relationship and, in the publications referred to here, the authors generally use the specific permeability, K, as a means of communicating their conclusions relative to their measured pressure drop data [3]. Thus, we may write as follows:

$$\mathrm{K} = \frac{\mu_s \eta \mathrm{L}}{\Delta P} \tag{4}$$

Where, K = the specific permeability.

Accordingly, we can see from equation (4) that this methodology differs from that of using the hydraulic gradient because it does not contain a term representing the kinetic contributions to pressure gradient, being confined to viscous contributions only. Consequently, it does not contain specific terms for, either the fluid density, ρ_f, or the acceleration due to gravity, g, both of which are readily available from reference text books and are, more importantly, embedded in the pressure flow relationship, as dictated by the *Laws of Nature*.

The Kozeny/Carman Fluid Flow Model

Since many authors report their experimental results in terms of the so-called Kozeny constant, K_c, we include herein a definition as follows [4]: Thus, we may write, based upon the Kozeny-Carman equation:

$$K_c = \frac{\varepsilon_0^3 d_p^2}{K(1-\varepsilon_0)^2} \tag{5}$$

Where, ε_0 = the external porosity of the packed conduit, d_p = the spherical particle diameter equivalent, K_c = the Kozeny constant.

Accordingly, we can see that the Kozeny/Carman equation, similar to Darcy's Law, does not contemplate kinetic contributions to pressure gradient.

We have now defined a methodology based upon the well-settled theory taught by Forchheimer (1901) of evaluating the values reported by authors who suggest that the value of the Kozeny constant is a variable. By comparing the calculated value for K_c, using equation (5), in conjunction with the teaching of the Forchheimer model, therefore, we can debunk this erroneous methodology using the authors own measured values. We point out here that the Forchheimer model is even older than the Kozeny/Carman model by about 30 years [5]. Importantly, equation (5) contains the measured values for both ε_0 and d_p, both of which are very difficult to measure accurately when using UHPLC columns which contain the so-called sub 2 μm particles. In addition, these two parameters are not independent variables in the pressure flow relationship, as dictated by the Laws of Nature. Accordingly, using specific permeability K, as a means to communicate one's measured data, a practitioner is using the underlying variables of D, L, q, ΔP, η, ε_0 and d_p, which represents only 6 independently determined variables, since the latter two are dependent variables. To make matters even worse, when using this methodology to report their empirical results, these authors *never* reconcile their values for the latter two parameters, a prerequisite dictated by the Laws of Nature, and accordingly, their respective values are many times self-contradictory. Furthermore, since the viscosity term, η, is linearly related to pressure gradient, ΔP/L, via the fluid flux term (first power), μ_s, and the fluid density term ρ_f, is quadratically related to the pressure gradient via the fluid flux term (second power), reporting one's empirical results using the hydraulic gradient, j, is significantly more accurate, especially at higher values of fluid flux.

However, identifying these built-in errors as a result of choosing to ignore kinetic contributions in the pressure flow relationship, is just a first step, since it will only establish that the authors values are wrong and that, consequently, any conclusions or extrapolations based upon their erroneous values for K_c will be without merit. Accordingly, a second step is needed to correct for this invalid methodology which will correct for these mistakes, not only, with respect to identifying the unique value for K_c, but also, with respect to the measurement uncertainty relative to both these two latter terms. Fortunately, such a methodology was published for the first time in 2019, which we will take advantage of in this paper.

The Ergun Fluid Flow Model

Published circa 1950 by Ergun et al, this fluid flow model contains both a viscous and a kinetic term in its rendition of the pressure flow relationship [6]. Accordingly, it is a far more accurate methodology to capture the pressure flow relationship over the entire fluid flow regime from laminar to fully turbulent, than either Darcy's law or the Kozeny/Carman equation. Thus, we may write the Ergun equation as follows:

$$\frac{\Delta P}{L} = \frac{A(1-\varepsilon_0)^2\mu_s\eta}{\varepsilon_0^3 d_p^2} + \frac{B(1-\varepsilon_0)\mu_s^2\rho_f}{\varepsilon_0^3 d_p} \tag{6}$$

Where A and B are dimensionless coefficients.

Additionally, based upon the teaching of the Ergun fluid flow model, we may also write:

$$R_{em} = \frac{\mu_s d_p \rho_f}{\eta(1-\varepsilon_0)} \tag{7}$$

Where, R_{em} = the modified Reynolds number.

Despite the appropriate configuration of the Ergun equation and its merits to our application herein, however, it has been adequately documented in the literature that the values of 150 and 1.75 assigned by Ergun in 1952 for the values of A and B, respectively [7], are not accurate, and must be modified to accurately reflect the true relationship between the variables identified in equation (6) [8]. We will follow this approach herein and take advantage of modifying the Ergun equation values of A and B to present our QFFM analysis in a format recognizable to those not yet familiar with the teaching of the QFFM.

The Quinn Fluid Flow Model (QFFM)

This newly minted flow model was first published in 2019 under the label of "Quinn's Law of Fluid Dynamics in Closed Conduits" [9]. Since a detailed discussion of this development is beyond the scope of this paper, we will simply include some additional references herein to further assist the reader in understanding its impact and we will use it to correct for mistakes made by the authors under these circumstances [10-12]. For our needs here in this paper, we will simply adopt the teaching of the QFFM in the form of the Q-Modified-Ergun equation which defines the values of the Ergun coefficients of A and B based upon empirical evidence from the published papers. Thus, we may write from the QFFM, a definition for both Ergun coefficients as a function of the Forchheimer coefficients as follows:

$$\mathrm{A} = \frac{a_{For}\rho_f g d_p^2 \varepsilon_0^3}{\eta(1-\varepsilon_0)^2} \tag{8}$$

$$\mathrm{B} = \frac{b_{For}\rho_f g d_p \varepsilon_0^3}{(1-\varepsilon_0)} \tag{9}$$

Thus, we can see from equations (8) and (9) that our methodology includes specific terms for fluid density, ρ_f, and the acceleration due to gravity, g, which differentiates our methodology from that of the proponents of this variable Kozeny constant "mythology".

A Note of Clarification

We want to clarify what the QFFM teaches relative to the Ergun parameters of A and B. The QFFM is a flow model which is based upon first principles as well as empirical evidence. Therefore, it is a theoretical equation, which has been, nevertheless, validated over the entire fluid flow regime by using classical empirical studies both for packed and empty conduits. Accordingly, it teaches values for the

Forchheimer coefficients *equivalent* which are based upon theoretical underpinnings as well as those which are empirically derived. Thus, we may write from the QFFM, a definition for both Ergun coefficients as a function of theoretical underpinnings as follows:

$$A = \frac{256\pi}{3} \tag{10}$$

$$B = \frac{\lambda}{2\pi\varepsilon_0^3} \tag{11}$$

The QFFM defines the term λ as a wall effect normalization coefficient which, in the case of UHPLC columns, is always unity (λ=1), because there are no wall effects as a result of the very large D/d_p ratios in these packed conduits. This feature of the QFFM differentiates it from all other fluid flow models extant. Thus, it is abundantly clear from equations (10) and (11) that the value of A has always the constant value of 268.19 (approx.) and that the value of B is variable, being a function of the values of both λ and ε_0, the wall-effect normalization coefficient and external porosity of the packed conduit, respectively.

Finally, we point out that the values for both *Ergun* parameters, A and B, taught by the *QFFM*, are identical whether they are based upon the empirical *Forchheimer* coefficients [equations (8) and (9)] or the theoretical coefficients [equations (10) and (11)], allowing for measurement error in the former category. In other words, when properly adopted, all three fluid flow models, i.e., Forchheimer, Modified Ergun and QFFM, reinforce one another.

3. Evaluating Third Party Published Works

Example 1. Gritti et al 2014

In a paper published in the Journal of Chromatography A, the authors report on the performance of 4 UHPLC columns, i.e., the so-called sub-2 µm particle chromatographic columns [13]. The authors assert that each of the four columns have a different value for K_c, the Kozeny constant. In Table 1 of the paper, the authors report their experimentally derived values which also includes their back-calculated values [using their eq (20)] of 158, 164, 140 and 182, for the Kozeny constant for each of the 4 columns, respectively.

We have applied the Forchheimer model, as described above, to the authors measured data and include an analysis summary in our Tables below which contains all the measured data reported and a comparison of all fluid flow models mentioned above, i.e., Forchheimer, Kozeny/Carman, Q-Modified Ergun and QFFM.

Analysis Summary Gritti et al.

Table 1. *The raw measured data in Gritti et al.*

Sample	π	g	D	L	q	η	ρ_f	ΔP	K	Forchheimer				Kozeny	QFFM			Q-M-Ergun	
ID										j_{meas}	a_{For}	b_{For}	j_{For}	K_c	λ	ε_0	d_p	A	B
Measured																			
3193	3.14	981	0.21	10	0.008	0.006	0.90	300	4.E-05	33,979	153,500	80.15	33,979	268	1.00	0.41	2.E-04	268	2.23
3086	3.14	981	0.30	10	0.014	0.006	0.90	300	4.E-05	33,979	166,000	90.10	33,979	268	1.00	0.41	2.E-04	268	2.35
-3	3.14	981	0.21	50	0.001	0.006	0.90	300	4.E-05	6,796	172,500	95.70	6,796	268	1.00	0.40	2.E-04	268	2.42
-1	3.14	981	0.30	50	0.003	0.006	0.90	300	4.E-05	6,796	174,000	96.90	6,796	268	1.00	0.40	2.E-04	268	2.43

Table 2. *Flow Models for the reported data in Gritti et al. based upon the values for K_c.*

Sample	π	g	D	L	q	η	ρ_f	ΔP	K	Forchheimer				Kozeny	QFFM			Q-M-Ergun	
ID										j_{meas}	a_{For}	b_{For}	j_{For}	K_c	λ	ε_0	d_p	A	B
Reported																			
3193	3.14	981	0.21	10	0.008	0.006	0.90	300	4.E-05	33,979	153,488	137.00	33,979	158	1.00	0.39	2.E-04	158	2.67
3086	3.14	981	0.30	10	0.014	0.006	0.90	300	4.E-05	33,979	165,988	149.00	33,979	164	1.00	0.38	2.E-04	164	2.79
-3	3.14	981	0.21	50	0.001	0.006	0.90	300	4.E-05	6,796	172,500	198.00	6,796	140	1.00	0.37	2.E-04	140	3.16
-1	3.14	981	0.30	50	0.003	0.006	0.90	300	4.E-05	6,796	174,000	134.00	6,796	182	1.00	0.39	2.E-04	182	2.65

Table 3. *The QFFM corrected data in Gritti et al.*

Sample	π	g	D	L	q	η	ρ_f	ΔP	K	Forchheimer				Kozeny	QFFM			Q-M-Ergun	
ID										j_{meas}	a_{For}	b_{For}	j_{For}	K_c	λ	ε_0	d_p	A	B
QFFM																			
3193	3.14	981	0.21	10	0.008	0.006	0.90	300	4.E-05	33,979	153,500	80.15	33,979	268	1.00	0.41	2.E-04	268	2.23
3086	3.14	981	0.30	10	0.014	0.006	0.90	300	4.E-05	33,979	166,000	90.10	33,979	268	1.00	0.41	2.E-04	268	2.35
-3	3.14	981	0.21	50	0.001	0.006	0.90	300	4.E-05	6,796	172,500	95.70	6,796	268	1.00	0.40	2.E-04	268	2.42
-1	3.14	981	0.30	50	0.003	0.006	0.90	300	4.E-05	6,796	174,000	96.90	6,796	268	1.00	0.40	2.E-04	268	2.43

As shown in Table 1, we have determined both Forchheimer coefficients, a_{For} and b_{For} for each of the 4 columns measured by the authors. Note that the values identified for the b_{For} coefficient are, 80.15, 90.1, 95.7 and 96.9 for each of the 4 columns, respectively. Note also, the measured values for all 8 independent variables are displayed for each column reported.

In order to establish the methodology used by the authors to back-calculate their respective values for K_c based upon their equation (20) outlined in their paper, we have included our Table 2. As shown in Table 2, the values for the Forchheimer coefficients corresponding to the authors reported values for K_c for each of the 4 columns, are entirely different from the values shown in our Table 1 representing the measured data and having the same values for hydraulic gradient j. Note, in particular, that the values identified for the b_{For} coefficient are, 137, 146, 198 and 134 for each of the 4 columns, respectively. These values are significantly larger than those provided by the measured data, Therefore, this proves conclusively that the author's measured data does not support their reported values for K_c.

In order to further explain and correct the errors contained in the authors methodology, we include our Table 3. As shown in Table 3, applying the QFFM to the authors measured data validates the measured values for both of the Forchheimer coefficients exactly. Furthermore, note that the back-calculated value for K_C, using the authors equation (20) establishes the unique value of 268 for all 4 columns. Note also, that the QFFM establishes different values for the underlying variables of ε_0 and d_p. In fact, the QFFM demonstrates that the author's values for these two measured parameters are about 10% too low.

In order to underline the significance of the authors erroneous methodology, we will now compare it to the corrected QFFM methodology, extrapolated to higher fluid flux values. We show this comparison for Col# 3193 in Figure 2 below.

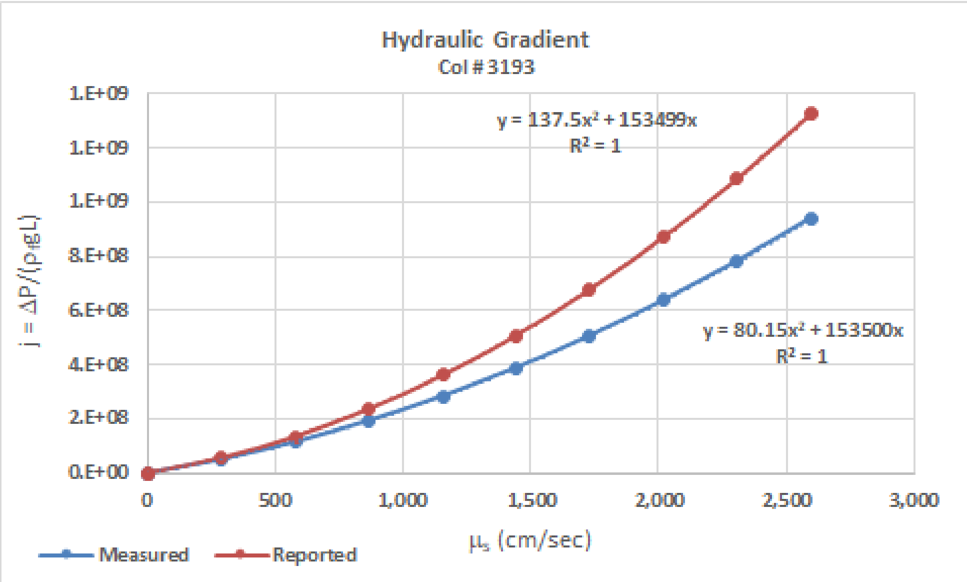

Figure 2. *Extrapolated data for Column # 3193.*

As shown in Figure 2, the authors methodology becomes more and more discrepant as the value of the fluid flux increases. In other words, the authors measurements were confined to very low values of the fluid flux where the hydraulic gradient is dominated by viscous contributions and where the contribution of the kinetic term is very small. However, had they made measurements at higher values of the fluid flux, where the kinetic term contribution is significant, their conclusions on the performance of the packed columns would be entirely different, as dictated by their own measurements and, consequently, the Laws of Nature.

Example 2. Cabooter et al 2008

In a paper published in the Journal of Chromatography A, the authors report on the performance of 6 UHPLC columns, i.e., the so-called sub-2μm particle chromatographic columns [14]. The authors assert that each of the six columns have a different value for K_c, the Kozeny constant. In their Table 2 of the paper, the authors report their experimentally derived values which also includes their back-calculated values [using their eq (6)] of 165, 151, 187 and 190, 123 and 117 for the Kozeny constant for each of the columns, respectively. In addition, in their Table 4 of the paper the authors report their back-calculated values [using their eq (6)] of 245, 239, 196 and 201, 179 and 179 for the Kozeny constant for each of the columns, respectively, but his time they use a different value for the particle size, d_p. Astonishingly, however, they use the same values for the external porosity, ε_0, in their back-calculation for both values for the particle diameter, d_p, which clearly establishes their underlying (erroneous) concept of treating these two variables as independent variables in the pressure flow relationship. In other words, they report 2 different values for d_p corresponding to the same values for ε_0 and measured pressure gradient, ΔP/L, which unambiguously violates the Conservation Laws of Nature.

We have applied the Forchheimer model, as described above, to the authors measured data and include an analysis summary in our Tables below which contains all the measured data reported and a comparison of all fluid flow models mentioned above, i.e., Forchheimer, Kozeny/Carman, (Q-Modified Ergun) and QFFM.

Analysis Summary Cabooter et al.

Table 4. The raw measured data in Cabooter et al.

Sample ID	Constants		Measured								Forchheimer			Kozeny	QFFM				Q-M-Ergun	
	π	g	D	L	q	η	ρ_f	ΔP	K	j_{meas}	a_{For}	b_{For}	j_{For}	K_c	λ	δ	ε_0	d_p	A	B
Measured-2																				
1-Hypersil	3.14	981	0.21	5	0.0004	0.008	0.71	1.E+07	3.44E-11	3,968	349,159	68	3,968	268	1.00	12	0.44	2.E-04	268	1.87
2-Hypersil	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	3.02E-11	4,528	398,449	82	4,528	268	1.00	13	0.43	2.E-04	268	2.03
3-Zorbax	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.59E-11	5,275	464,173	95	5,275	268	1.00	13	0.42	2.E-04	268	2.12
4-Zorbax	3.14	981	0.46	5	0.0004	0.008	0.71	4.E+06	2.65E-11	1,074	453,322	92	1,074	268	1.00	13	0.42	2.E-04	268	2.10
5-Acquity	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.61E-11	5,228	460,066	80	5,228	268	1.00	12	0.44	2.E-04	268	1.90
6-Acquity	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.44E-11	5,602	492,927	91	5,602	268	1.00	13	0.43	2.E-04	268	2.02

Table 5. The reported data in Cabooter et al. based upon the reported values for Kc shown in their Table 2.

Sample ID	Constants		Measured								Forchheimer			Kozeny	QFFM				Q-M-Ergun	
	π	g	D	L	q	η	ρ_f	ΔP	K	j_{meas}	a_{For}	b_{For}	j_{For}	K_c	λ	δ	ε_0	d_p	A	B
Reported-2																				
1-Hypersil	3.14	981	0.21	5	0.0004	0.008	0.71	1.E+07	3.44E-11	3,968	349,158	152	3,968	165	1.00	17	0.39	2.E-04	165	2.71
2-Hypersil	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	3.02E-11	4,528	398,449	213	4,528	151	1.00	20	0.37	2.E-04	151	3.16
3-Zorbax	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.59E-11	5,275	464,172	172	5,275	187	1.00	18	0.38	2.E-04	187	2.80
4-Zorbax	3.14	981	0.46	5	0.0004	0.008	0.71	4.E+06	2.65E-11	1,074	453,322	162	1,074	190	1.00	17	0.39	2.E-04	190	2.73
5-Acquity	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.61E-11	5,228	460,065	290	5,228	123	1.00	22	0.36	2.E-04	123	3.46
6-Acquity	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.44E-11	5,602	492,926	351	5,602	117	1.00	24	0.35	2.E-04	117	3.78

Table 6. The QFFM corrected data in Cabooter et al from their Table 2.

Sample ID	Constants		Measured								Forchheimer			Kozeny	QFFM				Q-M-Ergun	
	π	g	D	L	q	η	ρ_f	ΔP	K	j_{meas}	a_{For}	b_{For}	j_{For}	K_c	λ	δ	ε_0	d_p	A	B
QFFM-2																				
1-Hypersil	3.14	981	0.21	5	0.0004	0.008	0.71	1.E+07	3.44E-11	3,968	349,159	68	3,968	268	1.00	12	0.44	2.E-04	268	1.87
2-Hypersil	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	3.02E-11	4,528	398,449	82	4,528	268	1.00	13	0.43	2.E-04	268	2.03
3-Zorbax	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.59E-11	5,275	464,173	95	5,275	268	1.00	13	0.42	2.E-04	268	2.13
4-Zorbax	3.14	981	0.46	5	0.0004	0.008	0.71	4.E+06	2.65E-11	1,074	453,322	92	1,074	268	1.00	13	0.42	2.E-04	268	2.10
5-Acquity	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.61E-11	5,228	460,066	80	5,228	268	1.00	12	0.44	2.E-04	268	1.90
6-Acquity	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.44E-11	5,602	492,927	91	5,602	268	1.00	13	0.43	2.E-04	268	2.02

Table 7. The reported data in Cabooter at al based upon the reported values for Kc shown in their Table 4.

Sample ID	Constants		Measured								Forchheimer			Kozeny	QFFM				Q-M-Ergun	
	π	g	D	L	q	η	ρ_f	ΔP	K	j_{meas}	a_{For}	b_{For}	j_{For}	K_c	λ	δ	ε_0	d_p	A	B
Reported-4																				
1-Hypersil	3.14	981	0.21	5	0.0004	0.008	0.71	1.E+07	3.44E-11	3,968	349,159	125	3,968	245	1.00	17	0.39	2.E-04	245	2.72
2-Hypersil	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	3.02E-11	4,528	398,449	170	4,528	239	1.00	20	0.37	2.E-04	239	3.17
3-Zorbax	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.59E-11	5,275	464,172	168	5,275	196	1.00	18	0.38	2.E-04	196	2.80
4-Zorbax	3.14	981	0.46	5	0.0004	0.008	0.71	4.E+06	2.65E-11	1,074	453,322	157	1,074	201	1.00	17	0.39	2.E-04	201	2.72
5-Acquity	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.61E-11	5,228	460,065	242	5,228	179	1.00	22	0.36	2.E-04	179	3.47
6-Acquity	3.14	981	0.21	5	0.0004	0.008	0.71	2.E+07	2.44E-11	5,602	492,926	285	5,602	179	1.00	24	0.35	2.E-04	179	3.79

As shown in our Table 4, we have determined both Forchheimer coefficients, a_{For} and b_{For} for each of the 6 columns measured by the authors and reported in their Table 2.

In order to establish the methodology used by the authors to back-calculate their respective values for K_c based upon their equation (6) and reported in their Table 2, we have included our Table 5. As shown in our Table 5, the values for the Forchheimer coefficients corresponding to the authors reported values for K_c in their Table 2 for each of the 6 columns, are entirely different from the values shown in our Table 4 representing the measured data and having the same values for hydraulic gradient j. Note that the values for the b_{For} coefficient are significantly higher than those representing their measured data. Therefore, this proves conclusively that the author's measured data does not support their reported values for K_c in their Table 2.

Similarly, we use the QFFM in our Table 6 to, once again, identify the corrected value for K_c which the measured data supports. As shown in our Table 6, applying the QFFM to the authors measured data validates the measured values for both the Forchheimer coefficients exactly. Furthermore, note that the back-calculated value for K_C, using the authors equation (6) establishes the unique value of 268 for all 6 columns. Note also, that the QFFM establishes different values for the underlying variables of ε_0 and d_p. In fact, the QFFM demonstrates that the author's values for particle size is about 5% too large and the values for the external porosity are about 15% too low.

Finally, in order to establish the methodology used by the authors to back-calculate their respective values for K_c based upon their equation (6) and reported in their Table 4, we have included our Table 7. As shown in our Table 7, the values for the Forchheimer coefficients corresponding to the authors reported values for K_c for each of the 6 columns in their

Table 4, are entirely different from the values shown in our Table 4 representing the measured data and having the same values for hydraulic gradient j. Therefore, this proves conclusively that the author's measured data does not support their reported values for K_c reported in their Table 4.

In order to underline the significance of the authors erroneous methodology, we will now compare it to the corrected QFFM methodology, extrapolated to higher fluid flux values. We show this comparison for Col #1 Hypersil Gold C18 in Figure 3 below.

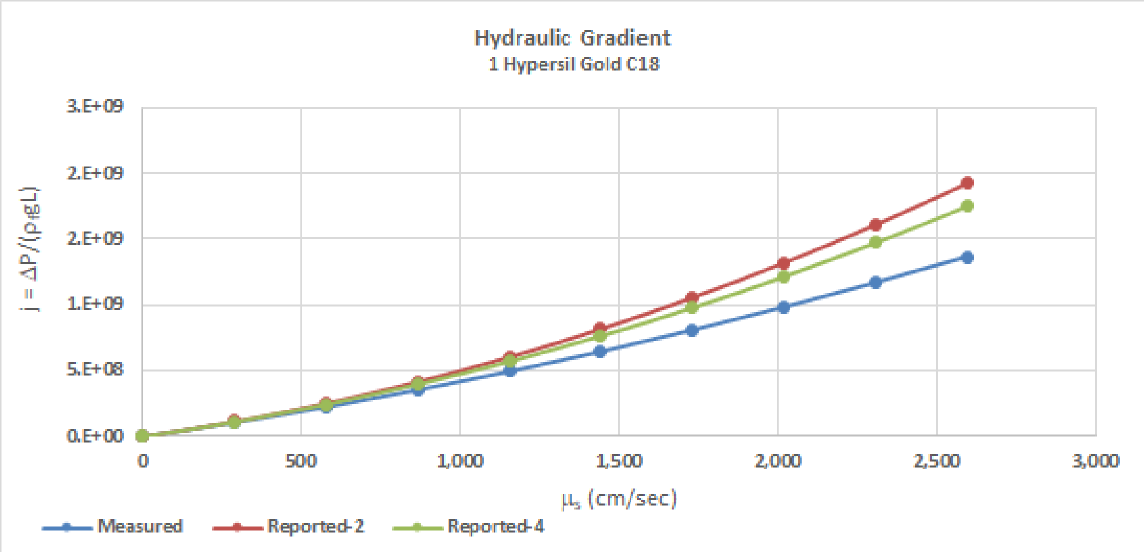

Figure 3. *Extrapolated data for Column # Hypersil Gold C18.*

As shown in Figure 3, the authors methodology becomes more and more discrepant as the value of the fluid flux increases. In other words, the authors measurements were confined to very low values of the fluid flux where the hydraulic gradient is dominated by viscous contributions and where the contribution of the kinetic term is very small. However, had they made measurements at higher values of the fluid flux, where the kinetic term contribution is significant, their conclusions on the performance of the packed columns would be entirely different, as dictated by their own measurements and, consequently, the Laws of Nature.

Finally, since the authors methodology has been shown herein to be invalid because it violates the Laws of Nature, on the one hand, and, on the other hand, demonstrates that their measurement technique used to identify the values of ε_o and d_p, was not sufficiently accurate, their proclamations regarding the relationship between reduced velocity, ν, and reduced plate height, h, both based upon these erroneous values, are null and void. The implications of this are significant but beyond the scope of this paper. We will further address this topic in a follow-on paper.

4. Conclusions

We have demonstrated in this paper that in order to validate the true value of the Kozeny constant, K_c, a practitioner must take measurements at both low and high values of the fluid flux parameter, μ_s, where the viscosity η, (low values of μ_s) and density ρ_f (high values of μ_s) of the fluid, and g, the acceleration due to gravity, are properly accounted for as dictated by the Laws of Nature and, consequently, the Navier-Stokes equation. Furthermore, we have shown that the errors in the authors methodology may be catalogued and explained as follows:

1. They used an invalid approximation for K_c which was too low by ignoring the kinetic term in their measured pressure/flow relationship. Rather, they based their calculated value for K_c on their inaccurately measured values of ε_o and d_p. This results in an *underestimation* of the viscous contributions to measured pressure drop and, by default, an overestimation of the kinetic contributions, even when the flow is laminar. In addition, because they treated the value of K_c as a variable across all the columns in the study, their miscalculations result in, not only, values for the viscous and kinetic contributions which are wrong, but also, values which are inherently inconsistent with respect to both contributions across the columns in the study.
2. Their measurement technique used to independently determine the values for ε_0 and d_p was not sufficiently accurate to identify the true values of these parameters in their experiments. For instance, the technique of Inverse Size Exclusion Chromatography (ISEC), which the authors used to determine the value of the external porosity is not capable of differentiating, with sufficient accuracy for use in the pressure flow relationship, the free space *between* the particles and the free space *within* the particles. This is, in part, due to the extraordinarily sensitive nature of the relationship between pressure drop and external porosity in a packed conduit which is amongst the most pronounced relationship found in all of physics.

3. Their methodology, erroneously, considers the parameters of external porosity, ε_o, and particle diameter, d_p, as independent variables in the pressure flow relationship. Accordingly, the authors did not reconcile their reported values for these two terms which is also a prerequisite dictated by the Laws of nature.
4. They ignored the Laws of Nature, a.k.a, (a) the Conservation Laws, (b) the Continuity Equation, (c) The Navier-Stokes equation, all of which dictate that, the values for ε_0 and d_p are not independent variables in the pressure flow relationship and, accordingly, must be reconciled as dependent variables, something the authors did not do.
5. The authors in the Gritti et al paper asserted as a footnote in Table 1 of their paper that they "measured" the permeability. This is a blatant misrepresentation. You cannot "measure" permeability, you can only "calculate" it. This is because permeability is a man-made entity, i.e., it is a mathematical construct, which has no basis in the Laws of Nature, unless it has been grounded (validated) by experiment, which the authors failed to do. Note that in our summary tables, herein, permeability, K, is designated as a calculated entity, not a measured one.

Conflict of Interest

The author has no conflict of interest, financial or otherwise, in this publication.

References

[1] Jan H. van Lopik1 • Roy Snoeijers1 • Teun C. G. W. van Dooren1 • Amir Raoof1 • Ruud J. Schotting; Transp Porous Med (2017) 120: 37–66 DOI 10.1007/s11242-017-0903-3.

[2] Forchheimer, P.: Wasserbewegung durch boden. Zeit. Ver. Deutsch. Ing 45, 1781–1788 (1901).

[3] H. Darcy, Les Fontaines Publiques de la Ville de Dijon, Victor Dalmont, Paris, France, 1856.

[4] J. Kozeny, "Ueber kapillare Leitung des Wassers im Boden." Sitzungsber Akad. Wiss., Wien, 136 (2a): 271-306, 1927.

[5] P. C. Carman, Trans. Instn. Chem. Engrs. Vol. 15, (1937) 155-166.

[6] Ergun, S. and Orning, A. A., Fluid Flow through Randomly Packed Columns and Fluidized Beds, Ind. Eng. Chem. vol. 41, pp. 1179, 1949.

[7] Ergun, S., Fluid Flow Through Packed Columns, Chem. Eng. Progr. vol. 48, pp. 89-94, 1952.

[8] Quinn H. M., A Reconciliation of Packed Column Permeability Data: Deconvoluting the Ergun Papers Journal of Materials Volume 2014 (2014), Article ID 548482, 24 pages http://dx.doi.org/10.1155/2014/548482

[9] Quinn, H. M., Quinn's Law of Fluid Dynamics; Pressure-driven Fluid Flow through Closed Conduits. Fluid Mechanics. Vol. 5, No. 2, 2019, pp. 39-71. doi: 10.11648/j.fm.20190502.12.

[10] Quinn, H. M., Quinn's Law of Fluid Dynamics: Supplement #1 Nikuradze's Inflection Profile Revisited. Fluid Mechanics. Vol. 6, No. 1, 2020, pp. 1-14. doi: 10.11648/j.fm.20200601.11.

[11] Quinn, H. M., Quinn's Law of Fluid Dynamics: Supplement #2 Reinventing the Ergun Equation. Fluid Mechanics. Vol. 6, No. 1, 2020, pp. 15-29. doi: 10.11648/j.fm.20200601.12.

[12] Quinn, H. M., Quinn's Law of Fluid Dynamics: Supplement #3 A Unique Solution to the Navier-Stokes Equation for Fluid Flow in Closed Conduits, Fluid Mechanics. Volume 6, Issue 2, December 2020, pp. 30-50. doi: 10.11648/j.fm.20200602.11.

[13] F. Gritti, D. S. Bell, Georges Guiochon, Particle size distribution and column efficiency. An ongoing debate revived with 1.9 µm Titan-C18 particles. Journal of Chromatography A 1355 (2014) 179-192.

[14] D. Cabooter, J. Billen, H. Terryn, F. Lynen, P. Sandra, G. Desmet. Detailed Characterization of the flow resistance of commercial sub-2 mm reversed-phase columns. Journal of Chromatography A 1178 (2008) 108-117.