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A moment method for analyzing breakthrough curves of step inputs

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Abstract. This paper presents a new and simple moment method for analyzing breakthrough curves for step inputs. An advantage of moment analyses, in general, is that the underlying physical model is not needed, unlike other techniques such as fitting convective (or advective) dispersion equations. Therefore moment calculations allow multispecies (such as partitioning tracers) to be considered in one, two, or three dimensions. Previous analyses using moments have emphasized the response for a pulse input. Generally, the travel (residence) time is of importance, and previous solution techniques do not perform well for long pulse or step inputs. In this paper the presented method is used to analyze breakthrough curves for step inputs, and the results are compared to fitted analytical solutions for the one-dimensional convection dispersion equation. Only negligible differences between the new moment method and the fitted analytical solutions are found for both simulated and experimental data. Superior performance over previous methods used for evaluating moments for step inputs is demonstrated.

1. Introduction

The most versatile approach to determining transport parameters in porous media is by moment methods [*Wakao and Kaguei*, 1982; *Jury and Roth*, 1990; *Leij and Dane*, 1991]. Results using moment analyses are more robust because an underlying physical model is not necessary. Applications can be made to "non-Fickian" processes [*Jury and Roth*, 1990] as well as to two- or three-dimensional systems, including those with partitioning to various phases of the soil-liquid system [*Jin et al.*, 1995]. By using these methods a breakthrough curve can be analyzed to obtain the mean breakthrough time and the degree of spreading. Traditionally, moment methods were only used with short pulse inputs because large integration errors are associated with long pulse inputs and because errors are exacerbated with higher-order moments [*Ostergaard and Michelsen*, 1969; *Anderssen and White*, 1971; *Wolff et al.*, 1979]. The moment method presented here expands this approach to step inputs, and this new method can also be used to obtain transport parameters for large pulse inputs.

The general mathematical form for moments:

$$m_n = \int_0^\infty t^n C(z, t)\, dt, \tag{1}$$

where m_n is the nth order time moment, C is concentration, and t is time (minutes). For high-order moments and large pulses this integral tends to put too much weight on the tailing portion of the curve, which has the highest errors for experimental data. For simplicity we use relative concentration and dimensional time for the moment analysis. The normalized moment is

$$M_n = \frac{m_n}{m_0} = \frac{\int_0^\infty t^n C(z, t)\, dt}{\int_0^\infty C(z, t)\, dt}, \tag{2}$$

and the nth central moment is

$$\mu_n = \frac{\int_0^\infty (t - M_1)^n C(z, t)\, dt}{\int_0^\infty C(z, t)\, dt}. \tag{3}$$

If the input signal is a delta function and C is the "flux" concentration, the expected arrival time (or mean breakthrough time) τ can be directly calculated from the first moment:

$$\tau(z) = M_1 = \frac{\int_0^\infty tC(z, t)\, dt}{\int_0^\infty C(z, t)\, dt}. \tag{4}$$

The variance μ_2, or second central moment, which is directly related to dispersion, can be determined from

$$\mu_2(z) = \frac{\int_0^\infty (t - \tau)^2 C(z, t)\, dt}{\int_0^\infty C(z, t)\, dt} = M_2 - M_1^2. \tag{5}$$

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To model solute movement through porous media, the convection (or advection) dispersion equation (CDE) is often used. The CDE describing axial dispersion of a conservative solute flow through a soil column under steady state condition is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z}, \quad (6)$$

where D is the dispersion coefficient (cm^2 min^{-1}); $v = q/\theta$, the average pore water velocity (cm min^{-1}); q is the Darcy water flux (cm min^{-1}); θ is the volumetric water content (cm^3 cm^{-3}); z is the distance downward (cm), and t is time (min). Equation (6) is satisfied by both a "residence" (volume-averaged) and a flux (flux-averaged) concentration [*Jury and Roth*, 1990]. Unlike the moment analysis, this equation is based on the assumption that the porous media and water content are homogeneous and isotropic.

To obtain v and D, column or field solute transport experiments are often performed to yield the observation data (breakthrough curves). On the basis of these breakthrough curves, v and D are often estimated using nonlinear regression. The most popular approach is the curve-fitting method, where transport parameters are determined by minimizing the sum of the squared differences between observed and fitted breakthrough curves. The CXTFIT code is representative of this approach [*Toride et al.*, 1995].

Using the moment method, pore water velocity and dispersion coefficient of the CDE can be directly calculated from the following expressions [*Kreft and Zuber*, 1978; *Wakao and Kaguei*, 1982; *Jury and Roth*, 1990; *Leij and Dane*, 1991]:

$$v = \frac{z}{M_1} \quad (7)$$

$$D = \frac{\mu_2 z v}{2\tau^2} = \frac{\mu_2 v^3}{2z}. \quad (8)$$

Mathematically, these results are for a delta input only and subject to [*Jury and Roth*, 1990]

$$C(z, 0) = 0, \quad (9)$$

$$C(0, t) = \delta(t), \quad (10)$$

$$C(\infty, t) = 0. \quad (11)$$

For the moment analysis of a breakthrough curve of a finite pulse input, *Wolff et al.* [1979] considered the CDE under the following initial and boundary conditions:

$$C(z, 0) = 0, \quad (12)$$

$$C(0, 0 \le t \le t_0) = 1, \quad (13)$$

$$C(0, t > t_0) = 0, \quad (14)$$

$$C(\infty, t) = 0. \quad (15)$$

The v and D of the CDE for a pulse input are

$$v = \frac{z}{M_1 - t_0/2} \quad (16)$$

$$D = \left(\mu_2 - \frac{t_0}{12}\right)\frac{v^3}{2z}, \quad (17)$$

where t_0 is the time used for a pulse input. However, this method is not appropriate for a large pulse because of the strong influence of tailing errors on D [*Wolff et al.*, 1979; *Wakao and Kaguei*, 1982]. Therefore it becomes advantageous to divide the experimental data of a large pulse into two sets of breakthrough curves under two step inputs: step increase and step decrease.

The initial and boundary conditions for a unit step increase input are (a similar approach can be used with a step decrease)

$$C(z, 0) = 0, \quad (18)$$

$$C(0, t) = u(t), \quad (19)$$

$$C(\infty, t) = 0. \quad (20)$$

The unit step function is defined by

$$u(t - t_0) = \begin{cases} 0 & t < t_0 \\ 1 & t > t_0 \end{cases}. \quad (21)$$

Leij and Dane [1991] analyzed breakthrough curves under step inputs. They redefined time moments using the complementary concentrations:

$$m_n = \int_0^\infty t^n[1 - C(t)]\, dt. \quad (22)$$

The expressions relating M_1 and μ_2 to D and v for the one-dimensional CDE assumptions are

$$M_1 = \frac{D}{v^2} + \frac{z}{2v} \quad (23)$$

$$\mu_2 = \frac{3D^2}{v^4} + \frac{zD}{v^3} + \frac{z^2}{12v^2}. \quad (24)$$

The purpose of this paper is to demonstrate a moment method for the step input through an alternative approach not typically used in the hydrological community. Furthermore, the utility and power of this method is demonstrated by comparing parameters obtained from this new method to those from an analytical solution of the CDE using CXTFIT. As an example, this method is demonstrated by evaluating M_1 and μ_2. The accuracy of this method is maintained with application to higher-order moments.

2. The Time Moment Method for Step Inputs

To analyze the breakthrough curves from a step input, we compared initial and boundary conditions for a delta input (equations (9)–(11)) and a unit step input (equations (18)–(20)). From a mathematical point of view a delta function is the derivative of a step function. Expressions for the delta function are

$$\delta(t - t_0) = 0 \qquad t \ne t_0 \quad (25)$$

$$\int_{-\infty}^{\infty} \delta(t - t_0)\, dt = 1. \quad (26)$$

The delta and unit functions are related by [*Jury and Roth*, 1990]

$$\frac{d[u(t - t_0)]}{dt} = \delta(t - t_0). \quad (27)$$

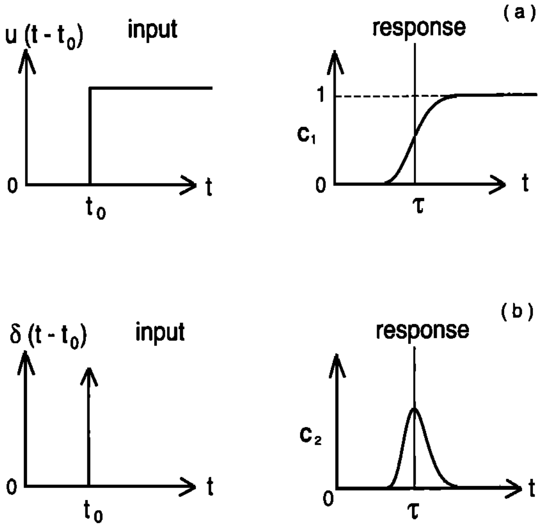

Figure 1. The relation between input functions and response functions for (a) step input and (b) delta (or impulse) input.

If two inputs are related by a linear operator, the outputs will be similarly related. Consider two sets of breakthrough data (see Figure 1), C_1 and C_2, obtained at the same location but in response to a step input (Figure 1a) and a delta input (Figure 1b), respectively. If the only difference between C_1 and C_2 is the method of introducing the tracer, then C_1 will be related to C_2 by

$$\frac{\partial C_1}{\partial t} = C_2. \tag{28}$$

This concept and mathematical expression have already been used by *Danckwerts* [1953], *Himmelblau and Dischoff* [1968], *Jury and Roth* [1990], *Kachanoski et al.* [1992], and *Elrick et al.* [1992].

As shown by (28), the derivative of the breakthrough curve obtained from a step input can be treated as the breakthrough curve obtained from a delta input. This can be used for moment analysis. The first moment M_1, which is the exact mean breakthrough time τ for the step input, can be expressed as

$$M_1 = \tau = \frac{\int_0^\infty t \frac{\partial C_1}{\partial t} dt}{\int_0^\infty \frac{\partial C_1}{\partial t} dt} = \frac{\int_0^1 t \, dC_1}{\int_0^1 dC_1} = \int_0^1 t \, dC_1, \tag{29}$$

with, i.e.,

$$\int_0^1 dC_1 = 1 \quad \text{for step increase.} \tag{30}$$

The second central moment, which is equivalent to the variance from a delta input, is

$$\mu_2 = \int_0^\infty (t - M_1)^2 \frac{\partial C_1}{\partial t} dt = \int_0^1 (t - M_1)^2 dC_1. \tag{31}$$

This method could be also extended to determine higher-order moments. The moments for a step input can thus be expressed as integrals with respect to concentration, unlike the previous moment methods, which are integrals with respect to time. According to (7) and (8) the v and D for the CDE equation can be calculated from M_1 and μ_2 values, which are obtained from (29) and (31).

3. Results and Discussion

To verify the moment expressions for step inputs for the one-dimensional CDE, i.e., (29) and (31), CXTFIT was used to predict breakthrough curves with varying parameters (see Table 1). The solution of (6) subject to type 1 boundary condition results in a flux concentration, assuming a constant flux input. Then, according to (29) and (31), M_1 and μ_2 were calculated by integrating the breakthrough curves using a trapezoidal rule. Parameters v and D were determined by (7) and (8). These values (τ, μ_2, v, and D) are presented in Table 1.

Table 1. Comparison Between Assumed and Calculated Parameters

Input Parameters[a]				Calculated Parameters			
z, L	Δt, T	v, $L\,T^{-1}$	D, $L^2\,T^{-1}$	τ, T	μ_2, T^2	v, $L\,T^{-1}$	D, $L^2\,T^{-1}$
10	0.25	1.0	0.1	0.1000×10^2	0.2005×10^1	0.1000×10^1	0.1003×10^0
50	0.50	1.0	0.1	0.5000×10^2	0.1002×10^2	0.1000×10^1	0.1002×10^0
100	0.80	1.0	0.1	0.1000×10^3	0.2005×10^2	0.1000×10^1	0.1003×10^0
200	1.20	1.0	0.1	0.2000×10^3	0.4012×10^2	0.1000×10^1	0.1003×10^0
500	2.00	1.0	0.1	0.5000×10^3	0.1003×10^3	0.1000×10^1	0.1003×10^0
100	0.1	1.0	0.001	0.1000×10^3	0.2008×10^0	0.1000×10^1	0.1004×10^{-2}
100	0.3	1.0	0.01	0.1000×10^3	0.2007×10^1	0.1000×10^1	0.1004×10^{-1}
100	0.8	1.0	0.1	0.1000×10^3	0.2005×10^2	0.1000×10^1	0.1003×10^0
100	2.0	1.0	1.0	0.1000×10^3	0.2003×10^3	0.1000×10^1	0.1002×10^1
100	7.0	1.0	10.0	0.1000×10^3	0.2004×10^4	0.1000×10^1	0.1002×10^2
100	600.0	0.01	0.1	0.1000×10^5	0.2003×10^8	0.1000×10^{-1}	0.1001×10^0
100	20.0	0.1	0.1	0.1000×10^4	0.2003×10^5	0.1000×10^0	0.1002×10^0
100	0.8	1.0	0.1	0.1000×10^3	0.2005×10^2	0.1000×10^1	0.1003×10^0
100	0.025	10.0	0.1	0.1000×10^2	0.2005×10^{-1}	0.1000×10^2	0.1003×10^0
100	0.0009	100.0	0.1	0.1000×10^1	0.2007×10^{-4}	0.1000×10^3	0.1003×10^0

Four decimal results are given for comparison purposes only.
[a]Predicted by CXTFIT.

Table 2. Comparison of Two Moment Methods for Step Inputs

			This Method			*Leij and Dane*'s [1991] Method		
z, L	v, $L\ T^{-1}$	D, $L^2\ T^{-1}$	τ, T	v, $L\ T^{-1}$	D, $L^2\ T^{-1}$	τ, T	v, $L\ T^{-1}$	D, $L^2\ T^{-1}$
10	1.0	0.05	10.0003	1.0000	0.0593	9.8894	1.0112	0.0886
20	1.0	0.05	20.0000	1.0000	0.0547	19.9441	1.0028	0.0690
30	1.0	0.05	30.0000	1.0000	0.0531	29.9626	1.0012	0.0626
40	1.0	0.05	40.0000	1.0000	0.0523	39.9720	1.0007	0.0594
50	1.0	0.05	50.0000	1.0000	0.0519	49.9775	1.0004	0.0575
60	1.0	0.05	60.0000	1.0000	0.0516	59.9813	1.0003	0.0563
80	1.0	0.05	80.0000	1.0000	0.0512	79.9860	1.0002	0.0547
100	1.0	0.05	100.0000	1.0000	0.0509	99.9887	1.0001	0.0538
120	1.0	0.05	120.0000	1.0000	0.0508	119.9906	1.0001	0.0531
10	1.0	0.1	10.0000	1.0000	0.1003	9.9969	1.0003	0.1011
50	1.0	0.1	50.0000	1.0000	0.1002	90.0002	0.5556	−3.0352
100	1.0	0.1	100.0000	1.0000	0.1003	220.0029	0.4545	−6.1471
200	1.0	0.1	200.0000	1.0000	0.1003	459.9987	0.4348	−12.2336
500	1.0	0.1	500.0000	1.0000	0.1003	1239.9946	0.4032	−30.0170

Four decimal results are given for comparison purposes only.

It can be seen that for the Δt we used, the calculated v and D from this new moment method are almost identical to the input parameters for CXTFIT (see Table 1). The calculated D has a relative error <0.4%.

To compare our moment method with the solution from *Leij and Dane* [1991], (equations (22), (23), and (24)), M_1 and M_2 were determined by integrating the following expression:

$$M_n(z) = \frac{\int_0^\infty t^n[1 - C(z, t)]\, dt}{\int_0^\infty [1 - C(z, t)]\, dt}, \qquad (32)$$

and μ_2 was calculated from

$$\mu_2 = M_2 - (M_1)^2. \qquad (33)$$

Then a quadratic equation was established for D/v^2 on the basis of (23) and (24). Parameters τ, v, and D can be solved from D/v^2 according to (23) since z is known. The comparison between these two moment methods is shown in Table 2. For $v = 1.0$ and $D = 0.05$ both methods gave good results for varying z values, though our method gives results closer to the input than those of *Leij and Dane* [1991]. For the other three sets of breakthrough data listed in Table 1 the method presented by *Leij and Dane* [1991] failed to give reasonable values.

To apply our moment method to experimental data, 10 breakthrough curves measured by time domain reflectometry (TDR) [*Yu*, 1998], including the step increase and step decrease inputs (see Figures 2a and 2b, respectively), were used. These breakthrough curves were analyzed for determination of

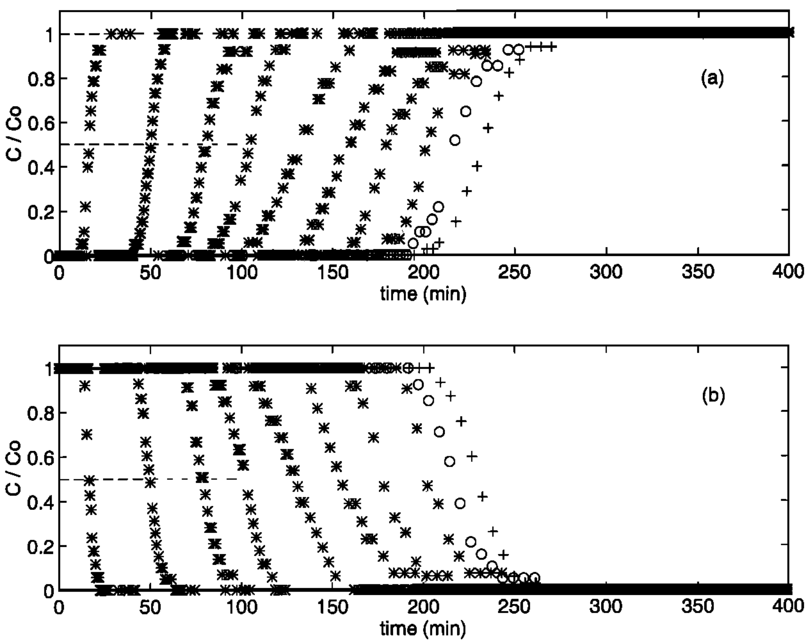

Figure 2. Breakthrough curves measured by 10 time domain reflectometry (TDR) probes for a flow rate of 8.0 $cm^3\ min^{-1}$ and an average θ_v of 0.267 for the top six layers (a) for step increase input and (b) for step decrease input.

v and D using our moment method. The results are presented in Table 3 for both step increase and step decrease inputs. For comparison, the CXTFIT code was applied for these breakthrough curves using resident concentrations under a "third-type" inlet condition. The fitted v and D are also presented in Table 3. Note that as expected, calculated v and D values vary depending on which depths are considered, both for the moment determination and from CXTFIT. To show more examples, data from *Toride et al.* [1995, Figure 7.3] were used. The results are presented in Table 4.

To investigate the effect of boundary conditions on the determination of v and D, we executed CXTFIT for these breakthrough curves under both the first- and the third-type conditions [*Toride et al.*, 1995]. The results are presented in Table 5; few noticeable differences are observed.

As mentioned, the CDE (equation (6)) can be used for the flux concentration C^f and the resident concentration C^r. The relationship between these two concentrations can be expressed as [*Jury and Roth*, 1990]:

$$C^f = C^r - \frac{D}{v}\frac{\partial C^r}{\partial z}. \tag{34}$$

The relationship between C^f and C^r is similar to the relationship between first-type and third-type boundary conditions. As expected, the differences between C^r and C^f are insignificant.

The nth time moment of (1) can be considered as multiplication of the concentration $C(z, t)$ by a weight t^n integrated under the breakthrough curve of a pulse input. When t is large, the weight t^n also becomes large. The weighting factor t^n therefore puts a large weight on the tailing part of the response curve where the relative experimental error is the greatest [*Ostergaard and Michelsen*, 1969; *Anderssen and White*, 1971; *Wolff et al.*, 1979]. In evaluating the central moments the errors are magnified not only for the tailing part but also for the early breakthrough part (equation (3)). These features cause large errors in parameter determination, though the method for a finite pulse input (equations (16) and (17)), theoretically, is as accurate as the method for a delta input. We combined the breakthrough curve from the individual step increase input with the curve from the step decrease input to form a large-pulse breakthrough curve (t_0 = 1385 min). The moment method from *Wolff et al.* [1979] was used to calculate v and D. It can be seen from Table 6 that the values of v are slightly smaller than the v obtained from CXTFIT, but D increases by 2 orders of magnitude. However, using the step increase and step decrease moment method for the same data (Table 3), it can be seen that our method yields values for v and D comparable to CXTFIT. Therefore the attempt to use the time moment for a large pulse is not practical. In fact, it is preferable to consider a large pulse as two step input experiments.

Table 3. Parameters Determined by Moments and CXTFIT

	From Moments				From CXTFIT	
Depth, cm	τ, min	μ_2, min^2	v, cm min^{-1}	D, cm^2 min^{-1}	v, cm min^{-1}	D, cm^2 min^{-1}
			Step Increase[a]			
6.5	16.7	11	0.390	0.0480	0.401	0.0368
18.0	49.9	20	0.361	0.0259	0.362	0.0264
30.5	81.4	100	0.375	0.0861	0.380	0.0648
42.5	104.1	111	0.408	0.0892	0.410	0.0949
54.5	132.4	280	0.412	0.1792	0.414	0.215
67.0	162.1	458	0.413	0.2413	0.420	0.217
79.0	186.1	465	0.425	0.2251	0.433	0.167
89.0	204.7	245	0.435	0.1131	0.438	0.107
94.0	219.2	260	0.429	0.1091	0.431	0.101
100.5	233.7	291	0.430	0.1154	0.432	0.101
			Step Decrease[b]			
6.5	16.8	5	0.386	0.0234	0.392	0.0258
18.0	50.0	23	0.360	0.0296	0.363	0.0281
30.5	79.5	52	0.384	0.0479	0.387	0.0489
42.5	101.4	82	0.419	0.0707	0.419	0.0777
54.5	129.9	210	0.419	0.1428	0.422	0.177
67.0	158.5	301	0.423	0.1698	0.428	0.162
79.0	180.3	207	0.438	0.1104	0.441	0.101
89.0	206.1	224	0.432	0.1012	0.436	0.0795
94.0	218.2	257	0.431	0.1095	0.434	0.0886
100.5	230.3	177	0.436	0.0726	0.437	0.0729

[a]NaCl solution from 20 to 35 mM.
[b]NaCl solution from 35 to 20 mM.

Table 4. Parameters Determined by Moments and CXTFIT

	From Moments				From CXTFIT[a]	
Depth, cm	τ, min	μ_2, min^2	v, cm min^{-1}	D, cm^2 min^{-1}	v, cm min^{-1}	D, cm^2 min^{-1}
			Step Increase			
11	4.518	0.2379	2.44	0.156	2.45	0.154
17	6.807	0.3172	2.50	0.145	2.51	0.126
23	9.204	0.3518	2.50	0.119	2.51	0.110
			Step Decrease			
11	43.05	46.19	0.256	0.0350	0.258	0.0357
17	67.04	90.90	0.254	0.0436	0.254	0.0393
23	92.43	135.8	0.249	0.0455	0.249	0.0429

[a]From *Toride et al.* [1995].

4. Conclusions

As with other moment analyses, an advantage of method presented is that no underlying physical model is needed for calculating the travel times and results can be used for a conservative or partitioned species and for two- and three-dimensional processes. The new contribution is that inputs can be a step function input or a long finite pulse and results are generally more accurate than those previously available. Using the special case of one-dimensional convective (or advective) dispersion, results compared favorably with those using the nonlinear regression in CXTFIT [*Toride et al.*, 1995]. In order

Table 5. Comparison of Parameters Determined by CXTFIT Under Type 1 and Type 3 Boundary Conditions

	First Type		Third Type	
z, cm	v, cm	D, cm min^{-1}	v, cm	D, cm min^{-1}
		Step Increase		
11	2.44	0.153	2.45	0.154
17	2.51	0.126	2.51	0.126
23	2.51	0.110	2.51	0.110
		Step Decrease		
11	0.255	0.0355	0.258	0.0357
17	0.254	0.0393	0.254	0.0393
23	0.249	0.0428	0.249	0.0429

Table 6. Parameters Determined From a Large Pulse

	From Moments[a]				From CXTFIT	
Depth, cm	M_1, min	μ_2, min^2	v, cm min^{-1}	D, cm^2 min^{-1}	v, cm min^{-1}	D, cm^2 min^{-1}
6.5	0.7563×10^3	0.2325×10^6	0.102	0.592×10^1	0.384	0.505×10^{-1}
18.0	0.7823×10^3	0.2223×10^6	0.201	0.140×10^2	0.358	0.336×10^{-1}
30.5	0.8077×10^3	0.2302×10^6	0.265	0.214×10^2	0.381	0.645×10^{-1}
42.5	0.8150×10^3	0.2189×10^6	0.347	0.290×10^2	0.412	0.924×10^{-1}
54.5	0.8370×10^3	0.2036×10^6	0.377	0.215×10^2	0.415	0.268×10^0
67.0	0.8684×10^3	0.2053×10^6	0.381	0.188×10^2	0.419	0.331×10^0
79.0	0.9068×10^3	0.2079×10^6	0.369	0.152×10^2	0.429	0.218×10^0
89.0	0.9782×10^3	0.2255×10^6	0.312	0.112×10^2	0.391	0.184×10^1
94.0	0.1016×10^4	0.2385×10^6	0.290	0.102×10^2	0.365	0.733×10^1
100.5	0.9773×10^3	0.2226×10^6	0.353	0.137×10^2	0.425	0.298×10^0

This large pulse is composed by combining step increase and step decrease inputs of Table 3 with t_0 = 1385 min.

[a]*Wolff et al.*'s [1979] method: v and D are calculated by (16) and (17).

to minimize the tailing error on determination of transport parameters we suggest that the breakthrough curve of a large pulse be divided into two step input breakthrough curves whenever a method of moments is used.

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