In situ estimation of the effective chemical diffusion coefficient of a rock matrix in a fractured aquifer

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Abstract An in situ method of estimating the effective diffusion coefficient for a chemical constituent that diffuses into the primary porosity of a rock is developed by abruptly changing the concentration of the dissolved constituent in a borehole in contact with the rock matrix and monitoring the time-varying concentration. The experiment was conducted in a borehole completed in mudstone on the campus of the University of the Free State in Bloemfontein, South Africa. Numerous tracer tests were conducted at this site, which left a residual concentration of sodium chloride in boreholes that diffused into the rock matrix over a period of years. Fresh water was introduced into a borehole in contact with the mudstone, and the time-varying increase of chloride was observed by monitoring the electrical conductivity (EC) at various depths in the borehole. Estimates of the effective diffusion coefficient were obtained by interpreting measurements of EC over 34 d. The effective diffusion coefficient at a depth of 36 m was approximately 7.8×10^{-6} m^2/d, but was sensitive to the assumed matrix porosity. The formation factor and mass flux for the mudstone were also estimated from the experiment.

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Résumé Une méthode in situ d'estimation du coefficient effectif de diffusion pour un composé chimique qui diffuse dans la porosité primaire d'une roche est développée, en modifiant brusquement la concentration du composé dissous dans un forage en contact avec la matrice rocheuse et en suivant l'évolution de sa concentration dans le temps. L'expérimentation a été réalisée dans un forage équipé dans des argilites sur le campus de l'Université de l'Etat Libre de Bloemfontein (Afrique du Sud). Plusieurs essais de traçage ont été réalisés sur ce site, laissant des concentrations résiduelles en hypochlorite de sodium dans les ouvrages, qui ont diffusé dans la matrice rocheuse au fil des années. De l'eau douce a été injectée dans un forage en contact avec les argilites, et l'augmentation temporelle de la concentration en chlorures a été observée par des mesures étagées de conductivité. L'estimation du coefficient effectif de diffusion est issue de l'interprétation des mesures de conductivité sur une période de 34 jours. Le coefficient effectif de diffusion à 36 m de profondeur est estimé autour de 7.8×10^{-6} m^2/j, mais il apparaît sensible à la porosité évaluée. Le facteur de formation et le flux de masse issu des argilites ont également été estimés à partir de ce test.

Resumen Se ha desarrollado un método in situ para estimar el coeficiente de difusión efectivo para un constituyente químico que sufre difusión en la porosidad primaria de una roca mediante un cambio abrupto en la concentración del constituyente disuelto en un sondeo en contacto con la matriz de la roca y monitorizando la variación de la concentración en el tiempo. El experimento se desarrolló en un sondeo completo en arcillas en el campus de la Universidad de Free State en Bloemfontein, Sudáfrica. Se han llevado a cabo numerosos ensayos de trazadores en este punto, que ha dejado una concentración residual de cloruro sódico en sondeos que han sufrido difusión en la matriz de la roca durante un periodo de años. El agua dulce se introdujo en el sondeo en contacto con las arcillas, y se observó el incremento variable en el tiempo del cloruro mediante la monitorización de la Conductividad Eléctrica (EC) a varias profundidades en el sondeo. La estimación del coeficiente de difusión efectiva se obtuvo interpretando las medidas de EC durante 34 días. El coeficiente de difusión efectiva a una profundidad de 36 m fue aproximadamente de 7.8×10^{-6} m^2/d, pero fue sensible a la porosidad de la

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matriz asumida. El factor de formación y el flujo de masa para las arcillas también se estimaron a partir del experimento.

Keywords Diffusion · Fractured rocks · Groundwater flow · Matrix diffusion · South Africa

Introduction

In fractured-rock aquifers, fractures are the principal pathways through which most groundwater moves, and thus, fractures are responsible for the fluid advection and mechanical dispersion of dissolved constituents. Fractured-rock aquifers are also characterized by a primary porosity (or rock matrix), which is the intrinsic porosity of the rock upon its formation. In some crystalline rocks, the matrix porosity may range from less than 1 to greater than 3% (Wood et al. 1996); the matrix porosity of sedimentary rocks may be much higher (Finley and Tyler 1986; Mace and Hvorka 2000). In many instances, the permeability of the matrix porosity is not capable of transmitting significant quantities of fluid. The matrix porosity, however, can act as a fluid-filled reservoir in contact with the fluid in the fractures. Dissolved constituents may diffuse from fractures into the rock matrix or vice versa, depending on the direction of the concentration gradients.

In situations where contaminants have been introduced into the groundwater of fractured-rock aquifers, the diffusion and retention of chemical constituents in the rock matrix is a significant problem in the design and implementation of groundwater remediation strategies (Parker et al. 1994). Pumping may readily remove the contaminated groundwater from fractures, but the migration of the contaminants from the rock matrix to the fractures will be limited by chemical diffusion. In instances where contaminated groundwater in fractures has been in contact with the rock matrix for months, years, or decades, the time frame for the diffusion of contaminants out of the rock matrix may extend to hundreds of years (Robinson 1994). Quantifying the magnitude of the chemical diffusion into or out of the rock matrix in different types of fractured-rock aquifers is extremely important in managing water resources and designing groundwater remediation strategies.

The diffusion of a constituent dissolved in the groundwater of a rock matrix is governed by the following differential equation

$$\frac{\partial C}{\partial t} - D\nabla^2 C = 0 \tag{1}$$

where C is the concentration of the dissolved constituent per volume of water, t is time, D is the effective diffusion coefficient of the dissolved constituent in the fluid of the rock matrix, and ∇^2 is the Laplacian operator, which will take different forms depending on the coordinate system associated with the diffusion process. In Eq. (1), it is assumed that the chemical constituent under consideration is nonreactive with fracture surfaces and the rock matrix, and there is no fluid advection in the rock matrix. The effective diffusion coefficient, D, is dependent on the diffusion coefficient of the dissolved constituent in water and the pore structure of the rock matrix,

$$D = \phi D_{\mathrm{d}} \tag{2}$$

where D_{d} is the free-water diffusion coefficient of the dissolved constituent, and ϕ is the formation factor that scales the free-water diffusion coefficient to account for diffusion in the tortuous pore structure of the rock matrix. The formation factor is a dimensionless term that is less than 1 and can range over several orders of magnitude, depending on the type of rock under consideration (Novakowski and Van der Kamp 1996).

Ohlsson and Neretnieks (1995) summarized the results of numerous laboratory-scale diffusion experiments conducted in crystalline rocks and identified a range of formation factors and the effective diffusion coefficients for various chemical constituents. Van der Voort (2001) conducted laboratory-scale diffusion experiments in samples of sandstone, shale, and quartzite using NaCl and sodium sulfate (Na_2SO_4) as the tracing solutions. In addition, Van der Kamp et al. (1996) and Novakowski and Van der Kamp (1996) describe an experimental procedure and method of interpreting laboratory-scale radial diffusion experiments conducted on core samples.

Controlled in situ experiments conducted by injecting tracer solutions into fractures under forced hydraulic gradient conditions have also been used to estimate the magnitude of the effective diffusion coefficients (Garnier et al. 1985; Becker and Shapiro 2000). Such tests are usually conducted over distances of meters to tens of meters in the formation, and the tracer breakthrough curves are examined to estimate the effective diffusion coefficient and the formation factor.

In addition, concentrations of environmental tracers (e.g., tritium and chlorofluorocarbons) have been used to estimate the effective diffusion coefficient under in situ conditions. Environmental tracers are chemical constituents or dissolved gases that are entrained in precipitation and eventually recharge the groundwater (Maloszewski and Zuber 1991; Shapiro 2001). The application of environmental tracers, however, is used to infer the magnitude of the matrix diffusion over regional flow regimes that may extend over hundreds of meters to kilometers.

Methods of estimating the effective diffusion coefficient under laboratory conditions require a significant investment in precision equipment. Estimating the effective diffusion coefficient into or out of a rock matrix under in situ conditions (e.g., under forced hydraulic gradients, or from the interpretation of environmental tracers) can be greatly affected by the groundwater flow regime (Becker and Shapiro 2003; Shapiro 2001). In some instances, an effective matrix-diffusion coefficient that is greater than the free-water diffusion coefficient can arise as an artifact of the fluid velocity (Shapiro 2001).

This article describes a simple in situ tracer experiment conducted in a borehole in contact with the rock matrix to estimate the magnitude of the effective diffusion coefficient. The experiment considers the diffusion of a tracer into or out of the rock matrix along a section of a borehole that is in contact with intact unfractured rock. It is also assumed that there is no ambient borehole flow to disturb the distribution of the dissolved constituent in the borehole.

Methodology

The in situ tracer test described in this article was conducted at the Campus Test Site (CTS), located on the grounds of the University of the Free State in Bloemfontein, South Africa (Fig. 1). The CTS covers an area of approximately 34,200 m^2, and has been used as a facility to conduct various geophysical, hydraulic, and chemical transport investigations in fractured sedimentary rocks (Botha et al. 1998; Riemann 2002). The CTS consists of 35 percussion-drilled boreholes and nine core holes. All holes were vertically oriented with the exception of two core holes that were at an inclination of 45° to identify subvertical fractures.

The geology and hydrogeology of the site are discussed in Botha et al. (1998). In general, the site is characterized by four subhorizontal, sedimentary units. From land surface downward, these units are a mudstone, a carbonaceous shale, a sandstone, and a second mudstone unit. The thickness of each unit varies slightly in the boreholes at the CTS. Figure 2 shows a conceptual model of the vertical distribution of the sedimentary units at the site.

The top mudstone unit is unconfined and extends roughly to a depth of 14 m below land surface, and is characterized by a very low yield. The carbonaceous shale acts as an aquitard, separating the upper unconfined aquifer from the transmissive sandstone aquifer. The mudstone unit at the bottom of the sequence also has a low yield similar to the unconfined aquifer. The water levels associated with the aquifer units are schematically shown in Fig. 2. In general, the hydraulic heads in the upper and lower mudstone units are higher than the hydraulic head in the sandstone.

At the CTS, the transmissivity of the sandstone aquifer is dominated by a single, areally extensive subhorizontal bedding-plane fracture that intersects boreholes between approximately 20.0–23.0 m below land surface (Fig. 2). Van Tonder and Vermeulen (2005) estimated the transmissivity of the fracture to be about 580 m^2/d, whereas the transmissivity of the sandstone matrix was approximately 3 m^2/d. Subvertical fractures have also been detected in the sandstone, but they are regarded as being hydraulically insignificant because of their low transmissivity. Boreholes that intersect the sandstone and have open intervals below the bedding plane fracture are characterized by stagnant water below the fracture, as there are no detectable permeable features below the bedding-plane fracture in the sandstone.

Over the past decade, many tracer tests were conducted at the CTS (Van Wyk 1998; Riemann 2002), which

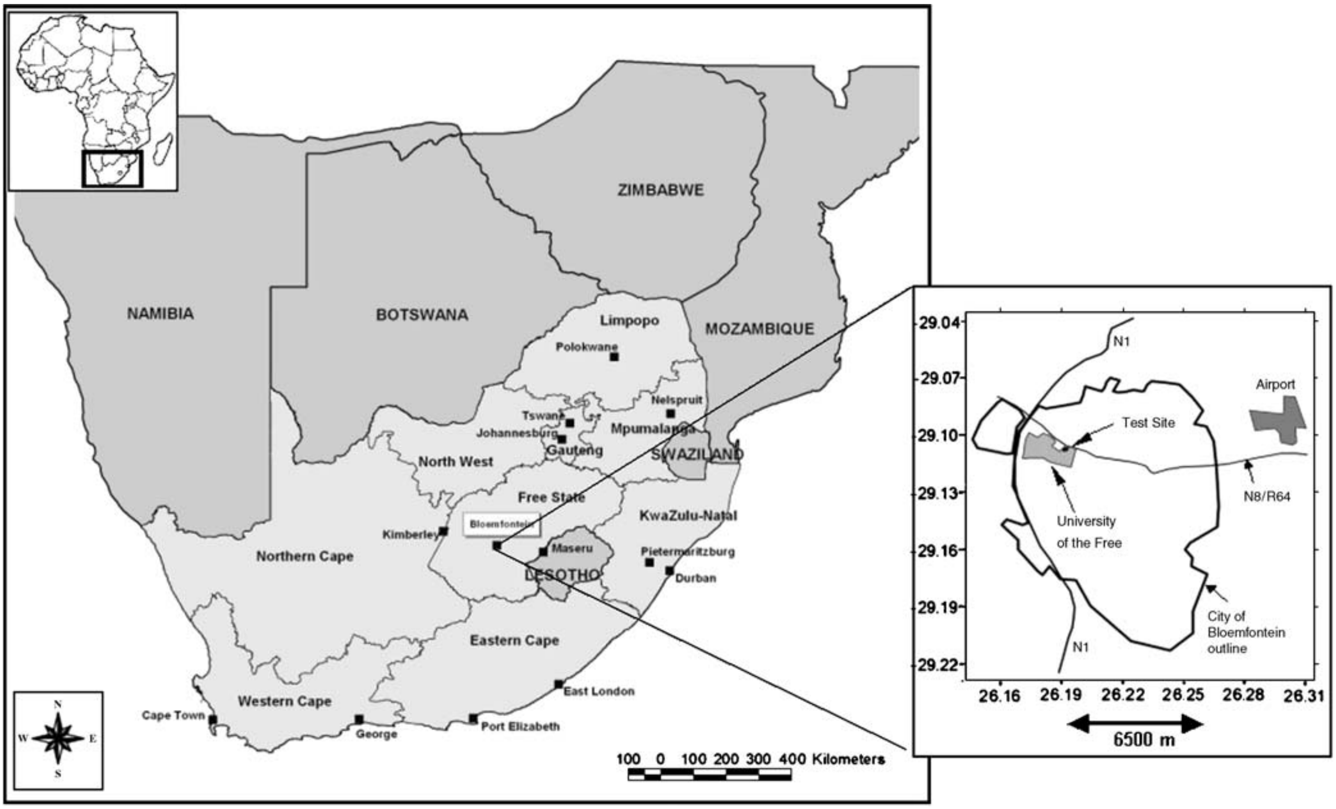

Fig. 1 Map of South Africa and the test site (coordinates in latitude and longitude)

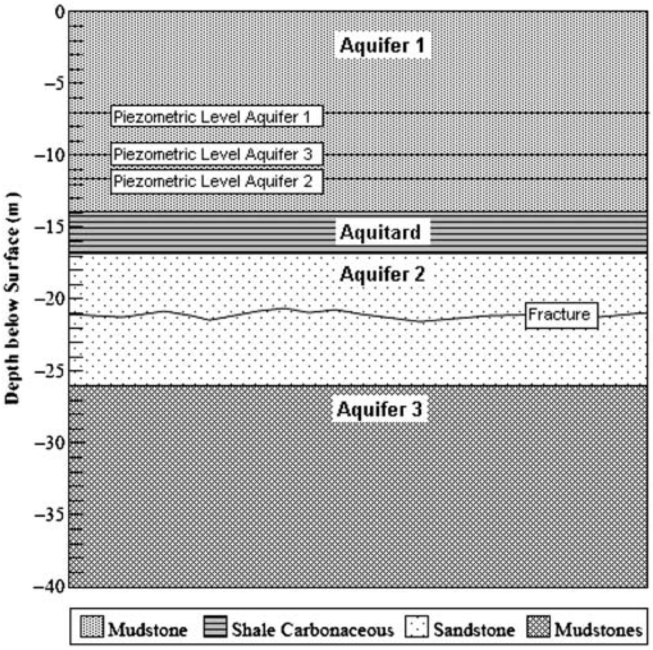

Fig. 2 Schematic diagram of the lithology and aquifers present at the Campus Test Site, University of the Free State, Bloemfontein, South Africa (after Botha et al. 1998)

involved numerous injections of tracers, in particular, NaCl. Although most of the tracer tests involved procedures to recover the injected tracer mass, a considerable amount of the residual tracer solution has remained in the stagnant fluid columns of some boreholes at the CTS and diffused into the rock matrix over time. Electrical conductivity (EC) surveys of boreholes at the CTS show elevated levels of dissolved constituents in sections of boreholes below the permeable subhorizontal, bedding-plane fracture in the sandstone. EC measurements as high as 2,900 mS/m have been recorded in the stagnant water of boreholes below the bedding-plane fracture. In contrast, the EC of water in the bedding-plane fractures is approximately 90 mS/m. The low EC in the bedding-plane fracture is indicative of fresh water recharging the aquifer and migrating in the most permeable feature of the formation.

Because water with high EC has been resident in the lower part of the borehole in contact with the rock matrix of the mudstone for an extended period, it is hypothesized that the concentration of the water in the rock matrix of the mudstone has equilibrated with the water in the borehole. The tracer test to estimate the effective diffusion coefficient of the mudstone matrix is conducted by introducing water into the lower part of the borehole that has low EC, and then monitoring the time-varying EC in the lower part of the borehole as a function of time. Alternatively, a test could be conducted by introducing a tracer solution in the borehole and monitoring its time-varying concentration as it diffuses into the rock matrix.

Borehole UO5, which intersects the bedding-plane fracture at a depth of 23.0 m, was selected for the in situ matrix-diffusion study. The diffusion experiment was conducted in the lower mudstone unit of this borehole, below the subhorizontal bedding-plane fracture in the sandstone. Observations from a downhole video camera in borehole U05 show no detectable fractures in the mudstone. Thus, changes in EC detected in the lower part of the borehole over time are assumed to be affected by chemical gradients between the fluid in primary porosity of the rock and the borehole. Although a regional upward hydraulic gradient is noted between the lower mudstone unit and the sandstone (Fig. 2), the absence of fractures in the lower mudstone unit in borehole U05, and the fact that the intrinsic porosity of the mudstone has extremely low permeability, implies that there is no fluid advection in the fluid column of the borehole.

Changes in the EC in the fluid column of borehole U05 were monitored with a Solinst TLC meter that was used to measure EC with depth in the borehole. Measurements were conducted by moving the probe up and down the borehole, while monitoring the depth of the probe with a tape accurate to 1 mm. Before the start of the test, EC measurements as a function of depth in the borehole were taken on 07 February 2005 (Fig. 3). The EC increases abruptly below the bedding-plane fracture in borehole U05 at approximately 23 m below land surface, indicating stagnant water in the borehole.

On 02 April 2005, a pump was placed at the bottom of borehole U05 (approximately 41 m below land surface) and the borehole was purged for 40 min at a rate of 1 L/s, after which the EC was measured as a function of depth in the borehole. As the borehole was purged, low salinity groundwater entered the borehole from the bedding-plane fracture at 23 m below land surface. Following the purging of the borehole, the EC was measured 9 times during the subsequent 34 d; measurements were stopped on 06 May 2005.

After purging the borehole, the concentration gradient is reversed with water having low EC residing in the borehole, whereas water in the adjacent rock matrix has higher EC. Consequently, solute in the fluid of the rock matrix starts to diffuse into the borehole in response to the concentration gradient. Table 1 lists the EC measured with time at depths of 27 and 36 m below land surface in borehole U05; this information is also shown graphically in Fig. 4. The first measurement was taken immediately after purging.

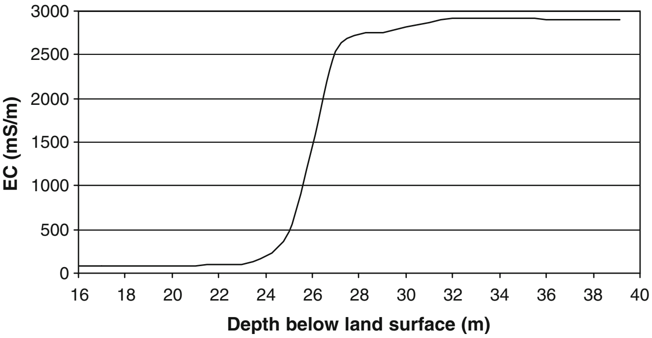

Fig. 3 EC versus depth in borehole UO5 on 7 February 2005 prior to the start of the in situ matrix diffusion experiment

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Table 1 EC measurements in borehole UO5 following the purging of the borehole on 2 April 2005

Date and Time	Elapsed time after purging, in days	EC, in mS/m, at 27 m below land surface	EC, in mS/m, at 36 m below land surface
02/04/2005 16:00	0	90.9	92.2
03/04/2005 10:30	0.8	97.1	100.1
03/04/2005 17:15	2.1	101.1	105.4
05/04/2005 15:16	3.0	102.1	108.4
06/04/2005 15:24	4.0	103.8	110.5
08/04/2005 14:05	5.9	105.4	113.6
13/04/2005 14:22	10.9	109.0	120.9
22/04/2005 08:47	19.7	112.9	130.5
06/05/2005 14:30	33.9	122.7	147.2

The increase in EC over time in borehole U05 (Fig. 4) is hypothesized to be the result of diffusion from the rock matrix into the borehole. The concentration with depth in the borehole prior to the start of the test is hypothesized to be the spatially varying concentration in the rock matrix with depth along the length of the borehole. EC values near the bedding-plane fracture at 23 m below land surface are not considered in the estimation of the matrix diffusion, because groundwater advection through the fracture may influence the EC in the borehole immediately adjacent to the fracture. After 34 d, the EC in the borehole at 27 m below land surface recovered from 90.90 to 122.70 mS/m, whereas at 36 m below land surface, the EC rose from 92.20 to 147.20 mS/m.

Discussion

The effective diffusion coefficient, D, is estimated by comparing the time-varying EC at locations in the borehole with the simulated responses from the solution to Eq. (1). In this analysis, EC is used as a surrogate for chloride concentration. Water samples were prepared in the laboratory with known chloride concentrations and EC measurements were taken. These experimental results showed that there is a direct correlation between chloride concentration and EC, where the chloride concentration in milligrams per liter is approximately four times the EC measured in milli-Siemens per meter. A similar correlation between EC and chloride concentration has also been reported by Hem (1989).

Because the EC measurements show variability with depth in the borehole, vertical concentration gradients in the fluid column of the borehole could affect the time-varying EC measurements in the borehole. It is anticipated that this phenomena would be greatest near the bedding-plane fracture, because water flowing in the bedding plane fracture has low EC resulting in a steep concentration gradient between the stagnant water in the fluid column in lower part of the borehole and the fluid in the bedding plane fracture. The potential effect of vertical concentration gradients on the estimates of the effective diffusion coefficient will be evaluated by comparing estimates of the effective diffusion coefficient at both 27 and 36 m below land surface.

Disturbances in the distribution of EC with depth in the borehole could also arise from lowering and raising the EC probe in the fluid column. This, however, is assumed to have a minimal effect on the EC distribution in the borehole, because the cross-sectional area of the probe is small relative to the diameter of the borehole. Thus, a minimal volume of fluid is displaced as the probe is moved in the borehole. Furthermore, EC measurements were taken infrequently over the duration of the test to avoid continuously disturbing the fluid column in the borehole.

In addition to examining the magnitude of the effective diffusion coefficient from the in situ experiment, the magnitude of the formation factor, ϕ, for the mudstone will be estimated by using Eq. (2) in combination with an estimate of the free-water diffusion coefficient for chloride. The formation factor is important in extending the results of this analysis to chemical constituents other than chloride. The results of the in situ experiment will also be used to examine the magnitude of the mass flux that results from diffusion.

Effective diffusion coefficient

The effective diffusion coefficient of the mudstone is estimated by interpreting the time-varying EC measurements at depths of 27 and 36 m in borehole UO5. To interpret the data shown in Fig. 4, the equations governing

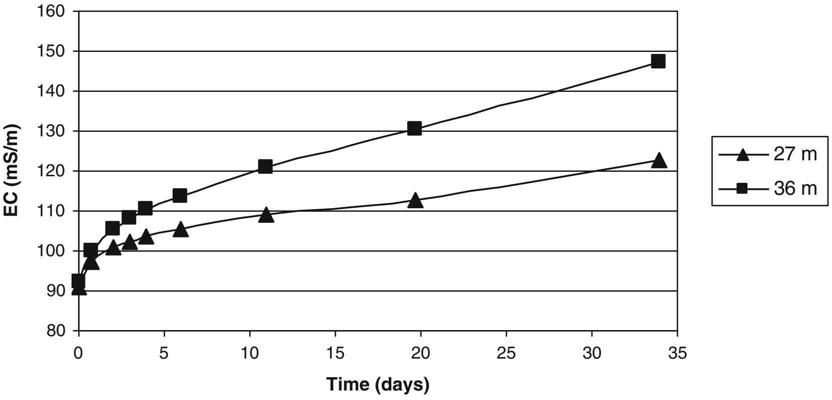


Fig. 4 EC measurements in borehole UO5 as a function of time at depths of 27 and 36 m below land surface following the purging of the borehole

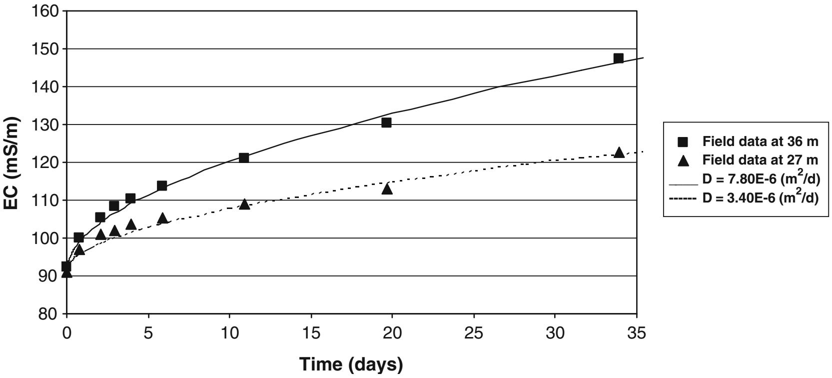


Fig. 5 Comparison of EC data from borehole U05 at 27 and 36 below land surface and model results for radial diffusion from the porous matrix to the borehole for different values of the effective diffusion coefficient; other model parameters are given in Table 2

the radial diffusion from the rock matrix to the borehole are solved. The equations governing the radial diffusion of a chemical constituent are given by Novakowski and Van der Kamp (1996). Following the approach of Novakowski and Van der Kamp (1996), the governing equations and the Laplace transform solution are given in the Appendix. From these equations, curves of EC versus time are generated, and the effective diffusion coefficient is varied so that model results best reproduce the measured time-varying EC values.

Typical solutions for EC in the borehole for different values of the effective matrix-diffusion coefficient are shown in Fig. 5. The physical parameters describing the borehole and the mudstone that were used to generate the curves in Fig. 5 are listed in Table 2. In the curves of concentration versus time shown in Fig. 5, a 1-m-long section of the borehole is assumed to represent the fluid volume in the borehole in contact with the rock matrix. Thus, the concentration in the rock matrix at a given elevation is assumed to be constant over a 1-m-long section of the borehole. The results in Fig. 5 show that larger effective diffusion coefficients result in a more rapid increase in the EC following the purging of the borehole.

The measured values of EC as a function of time at 27 and 36 m below land surface in borehole U05 are also plotted in Fig. 5. These data are compared to the modelled time-varying EC from the solution to radial diffusion into the borehole from the rock matrix to estimate the effective diffusion coefficients that best reproduce this data. The best fit for the EC data measured at 27 and 36 m below land surface are $3.4{\times}10^{-6}$ and $7.8{\times}10^{-6}$ m^2/day, respectively. The estimated effective diffusion coefficient at 27 m below land surface is approximately half the estimated effective diffusion coefficient estimated from the EC data at 36 m below land surface.

Table 2 Parameters assigned for model results of EC versus time at 27 and 36 m depths below land surface in borehole U05

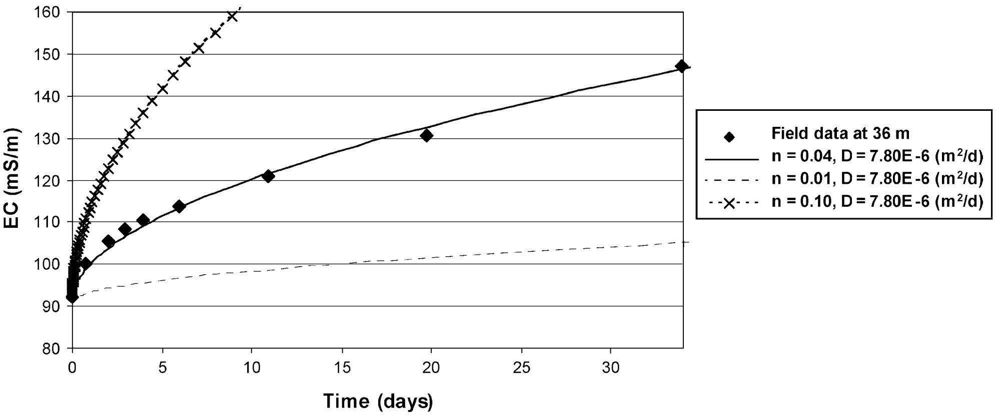
Depth	27 m	36 m
Average porosity of matrix	0.04	0.04
Initial EC (after purging)	91 mS/m	91 mS/m
EC in the matrix	2,540 mS/m	2,910 mS/m
Borehole radius	0.08 m	0.08 m
Length of borehole section	1 m	1 m
Borehole surface area	0.5 m^2	0.5 m^2
Borehole volume	0.02 m^3	0.02 m^3

The difference between the estimated effective diffusion coefficients at 27 and 36 m below land surface in borehole U05 could be the result of the vertical diffusion of chemical constituents in the borehole at the start of the test after purging. The difference between the effective diffusion coefficients estimated from the data at 27 and 36 m in the borehole could also be attributed to uncertainty in the matrix porosity. In the model calculations shown in Fig. 5, the porosity of the mudstone was assumed to be 0.04. Samples of lower mudstone unit from the vicinity of borehole U05 were not available to perform laboratory estimates of the matrix porosity. Estimates of the matrix porosity of the mudstone were conducted on samples from other locations in the same formation by Van der Voort 2001). Van der Voort (2001) observed the matrix porosity to vary between 0.01 and 0.10. Figure 6 shows the effect of varying the porosity of the mudstone from 0.01 to 0.10, while maintaining the effective diffusion coefficient estimated from the EC data at 36 m below land surface in borehole U05. Larger values of the matrix porosity result in more mass diffusion into the borehole and larger solute concentrations in comparison to model results using smaller values of the matrix porosity. Consequently, to reproduce the measured time-varying EC values assuming a smaller value of the matrix porosity requires a larger value of the effective matrix diffusion.

For the measured time-varying EC values in borehole U05 at 36 m below land surface, and an assumed mudstone matrix porosity of 0.01, the effective matrix-diffusion coefficient that best reproduces the data is $9.4{\times}10^{-5}$ m^2/d (Fig. 7). Also, for an assumed mudstone matrix porosity of 0.10, the effective diffusion coefficient that best reproduces the measured EC data at 36 m below land surface is $1.3{\times}10^{-6}$ m^2/d (Fig. 8). If variability in the matrix porosity is also considered in the evaluation of the time-varying EC data at 27 m below land surface in borehole U05, the estimates of the effective diffusion coefficient from the two elevations in the borehole overlap within the range of the sensitivity of the physical parameters.

In addition, it should also be noted that the time frame of the test over which the time-varying measurements of EC were made constitute only a small change in the EC relative to the assumed equilibrium values of EC in the

Fig. 6 Model results of EC versus time for different values of the matrix porosity and an effective diffusion coefficient of 7.8×10^{-6} m^2/d



borehole prior to the diffusion experiment. Consequently, the diffusion from the rock matrix to the fluid in the borehole has only impacted a small volume of the rock around the borehole. Over larger times, estimates of the effective diffusion coefficient may vary because the properties of the rock may not be uniform as a function of distance from the borehole. For example, drilling may have induced a change in stress in the vicinity of the borehole which has altered the porosity.

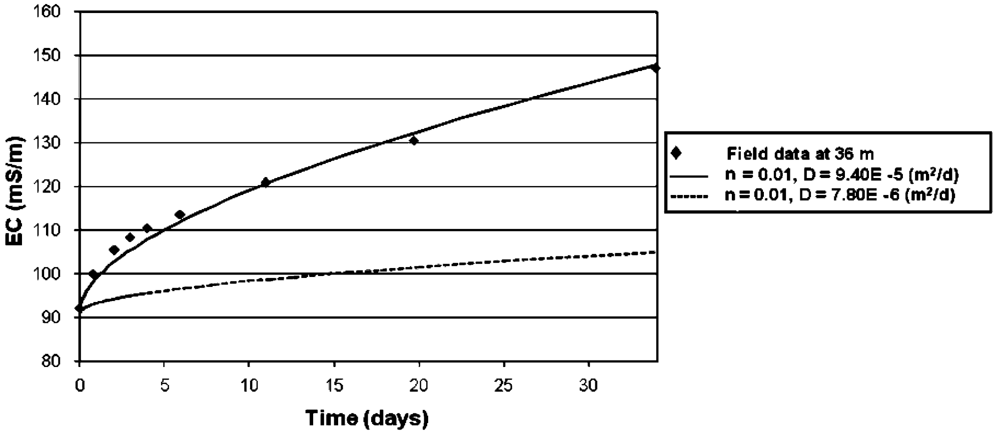
Formation factor

The effective diffusion coefficient is a combination of the free-water diffusion coefficient, D_d, for the dissolved constituent under consideration and a formation factor, ϕ, that scales D_d (see Eq. 2). If D_d is known, estimates of the formation factor, ϕ, can be obtained from estimates of the effective diffusion coefficient. Knowledge of the formation factor is important for extending the results of the in situ test to other dissolved constituents in the groundwater.

In this investigation, it is assumed that chloride is the principal component of the dissolved species in the groundwater causing the elevated values of EC. From the experimental results, it was found that the concentration of chloride (in mg/L) in the groundwater was equal to four times the EC (in mS/m). Values of EC in the borehole prior to the test at 27 and 36 m below land surface were 2,540 and 2,910 mS/m, respectively, which correspond to chloride concentrations of 10,160 and 11,640 mg/L chloride, respectively. The free-water diffusion coefficient for these concentrations of chloride in solution can be interpolated from the results given in Robinson and Stokes (1965). Robinson and Stokes (1965) give values of the free-water diffusion coefficient for sodium chloride solutions of various concentrations at 25°C. Correcting for the water temperature in the borehole, which was 18.9°C, the free-water diffusion coefficient for the chloride solution is estimated to be approximately 1.25×10^{-4} m^2/d at both 27 and 36 m below land surface in borehole U05.

Using the estimated free-water diffusion coefficient for the tracer solution, estimates of the formation factor from the time-varying EC measurements at 27 m below land surface range from 0.005 to 0.400, depending on the matrix porosity (Table 3). In contrast, the estimates of the formation factor from the time-varying EC measurements at 36 m below land surface range from 0.010 to 0.752 (Table 4). The estimates of ϕ at these elevations in the borehole overlap and could be the result of variability in the matrix porosity. Other authors have reported similar values for the formation factor from laboratory experiments conducted on other types of sedimentary rocks (see e.g., Novakowski et al. 1999), and a similar range in the formation factor is also found from laboratory experiments

Fig. 7 Estimates of the effective matrix diffusion coefficient from time-varying EC measurements at 36 m below land surface in borehole U05 for the matrix porosity of 0.01



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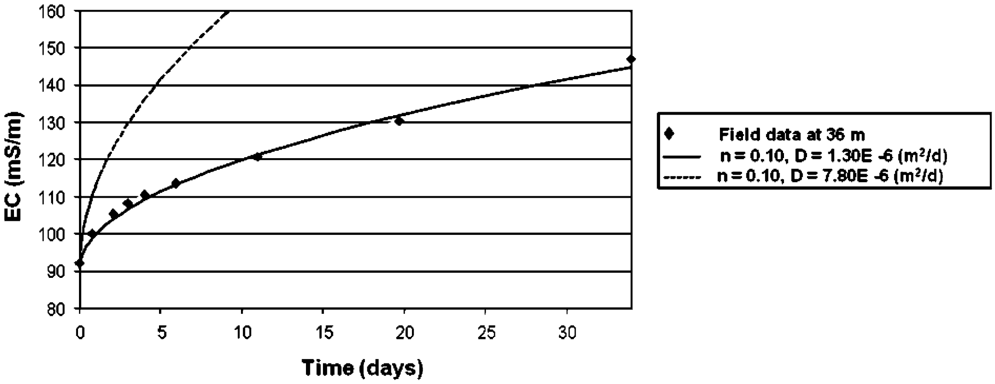

Fig. 8 Estimates of the effective matrix diffusion coefficient from time-varying EC measurements at 36 m below land surface in borehole U05 for the matrix porosity of 0.10

conducted on crystalline rocks (Ohlsson and Neretnieks 1995, 1997).

Mass flux

The Laplace transformation solution for the mass entering the borehole during the in situ test is given in Eq. (22). An inversion algorithm is used to estimate the chloride mass that enters the borehole from the rock matrix of the mudstone as a function of time. For the effective diffusion coefficient estimated from the EC data at 36 m below land surface in borehole U05, and an assumed matrix porosity of 0.04, approximately 4.4 mg of chloride enter the borehole over the 34 d of the test. These calculations are based on a conversion between EC and the chloride concentration noted previously. This calculation only considers a 1-m long section of the borehole. The total chloride mass that enters the borehole can be estimated by multiplying this result by the length of the borehole being considered in the experiment. If the length of the borehole associated with the experiment is assumed to be the distance from the bedding-plane fracture to the bottom of borehole U05, the total mass entering the borehole during the experiment is approximately 70.4 mg. In reality, the mass entering the borehole is a function of depth in the borehole, because of vertical concentration gradients. Thus, this estimate of total chloride mass entering over the entire length of the borehole should be regarded as an upper limit.

For comparison, the total mass in a volume of the rock matrix surrounding the borehole can also be calculated. If the initial chloride concentration measured in borehole U05 at 36 m below land surface is assumed to represent the chloride concentration in the rock matrix of the mudstone at the start of the test, 1 m^3 of the mudstone about the borehole contains approximately 4.7×10^5 mg chloride. In comparison, only 4.4 mg of chloride entered a 1-m section of the borehole over 34 d. Thus, over the time frame of the test, the diffusion of chloride into the borehole constitutes a minuscule mass of the chloride that is resident in the rock matrix adjacent to the borehole. One can use the solution for the mass entering the borehole given in the Appendix to extrapolate to later times. For example, after 100 d, 9 mg of chloride would enter the borehole, after 1,000 d, 29 mg of chloride would enter the borehole, and after 10,000 d, 103 mg of chloride would enter the borehole. Again, these calculations are for a 1-m-long section of the borehole.

These results illustrate the slow rate of diffusion into the borehole and the minimal amount of mass that will diffuse out of the rock matrix in response to perturbations in the concentration imposed in the borehole. At sites where there has been groundwater contamination and contaminants have diffused into the rock matrix, diffusion will be a limiting factor in remediating the groundwater. Estimates of mass removal from the rock matrix to fractures or boreholes can be made once the effective diffusion coefficient has been estimated.

Conclusion

A simple in situ method of estimating the effective diffusion coefficient associated with intact rock was designed and implemented in borehole completed in a mudstone on the grounds of the University of the Free State in Bloemfontein, South Africa. The method considers the abrupt change in the concentration of a constituent

Table 3 Estimates of the formation factor, ϕ, for estimates of the effective diffusion coefficient that best reproduce the measured EC at 27 m below land surface in borehole U05 for various values of the matrix porosity

Matrix porosity	Effective diffusion coefficient, m^2/d	Formation factor
0.01	5.0×10^{-5}	0.400
0.04	3.4×10^{-6}	0.027
0.10	6.0×10^{-7}	0.005

Table 4 Estimates of the formation factor, ϕ, for estimates of the effective diffusion coefficient that best reproduce the measured EC at 36 m below land surface in borehole U05 for various values of the matrix porosity

Matrix porosity	Effective diffusion coefficient, m^2/d	Formation factor
0.01	9.4×10^{-5}	0.752
0.04	7.8×10^{-6}	0.062
0.10	1.3×10^{-6}	0.010

in the fluid column of the borehole and the measurement of the time-varying concentration of that constituent. The fluid in the borehole is assumed to be stagnant such that diffusion into or out of the borehole is the only process affecting the change in the concentration of the constituent. In addition, the fluid column of the borehole is assumed to be in contact with the intact rock. Using a methodology similar to that given by Novakowski and Van der Kamp (1996), a solution for the time-varying concentration in the borehole was developed. For an assumed value of the formation porosity, the effective diffusion coefficient can be varied to best reproduce the time-varying concentration in the borehole.

In the illustration of this method discussed in this article, EC is used as a surrogate for the concentration of chloride in the formation. At the site under consideration, many tracer tests were conducted using sodium chloride over a period of years, which left a residual sodium chloride solution in the stagnant water at the lower part of many of the boreholes. In addition, the site was characterized by a single, highly conductive, subhorizontal, areally extensive bedding-plane fracture that was responsible for the majority of the groundwater flow. In boreholes that extend below this bedding-plane fracture, the water in the borehole was stagnant because of the absence of permeable fractures in the mudstone. The elevated values of EC over the length of the borehole below the bedding-plane fracture is assumed to be indicative of the concentration of chloride in the rock matrix of the mudstone.

The experiment was conducted by pumping water from the borehole which induced fresh water from the bedding-plane fracture to fill the bottom of the borehole. EC was then monitored as a function of time over the length of the borehole below the bedding-plane fracture. Estimates of the effective diffusion coefficient for the mudstone at two depths in the borehole were 3.4×10^{-6} and 7.8×10^{-6} m^2/d for an assumed matrix porosity of 0.04. The estimates of the effective diffusion coefficient, however, are sensitive to the assumed matrix porosity. A 20% change in the matrix porosity can alter the estimate of the effective diffusion coefficient by approximately a factor of two. In general, smaller estimates of the matrix porosity correspond to larger estimates of the effective diffusion coefficient.

The effective diffusion coefficient is a product of the free-water diffusion coefficient for the constituent under consideration and a formation factor. The formation factor scales the free-water diffusion coefficient to account for diffusion through the highly tortuous void space of the rock matrix. Identifying the formation factor is important in extending the results of the in situ diffusion experiment to other dissolved constituents. Using values of the free-water diffusion coefficient for chloride, the formation factor at two depths in the borehole were 0.027 and 0.062 for an assumed matrix porosity of 0.04.

The mass flux into or out of the borehole following the perturbation in the concentration of constituent in the borehole can be calculated from the solution for the time-varying concentration in the borehole. For the test described in this article, approximately 4.4 mg of chloride entered a 1-m-long section of the borehole from the formation over the 34 d of the test following the purging borehole with fresh water. In contrast, a cubic meter of rock around the borehole has approximately 4.7×10^5 mg of chloride. Only a minuscule mass of the chloride in the rock matrix adjacent to the borehole diffuses into the borehole over the time frame of the test. This illustrates that at sites with contaminated groundwater, the diffusion of contaminants out of the rock matrix can take an extended period of time.

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Appendix

The solution for the radial diffusion of a nonreactive solute from the rock matrix to a borehole is similar to the methodology given by Novakowski and Van der Kamp (1996) for a finite volume core sample. The mass balance equation for radial diffusion in the porous rock matrix is given by:

$$\frac{\partial c}{\partial t} - D\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) = 0 \tag{3}$$

where r is the radial coordinate measured from the centre of the borehole, c is the aqueous concentration (per unit fluid volume) in the porous matrix, t is time, D is the effective diffusion coefficient in the porous matrix for the chemical constituent under consideration, which is the product of the free-water diffusion coefficient for the constituent under consideration and a formation factor, which is inversely proportional to the tortuosity of the porous matrix, $D=\phi\ D_d$, where D_d is the free-water diffusion coefficient and ϕ is the formation factor.

The initial and boundary conditions associated with Eq. (3) are

$$c(r, t = 0) = C_m \tag{4}$$

$$c(r \to \infty, t) = C_m \tag{5}$$

$$c(r = R, t) = C_w(t) \tag{6}$$

where R is the radius of the borehole, C_m is the concentration in the porous matrix, which is assumed to be spatially uniform, and C_w is the concentration in the fluid column of the borehole, which is also assumed to be well mixed and uniform over the length of the borehole. Eq. (4) defines the initial concentration in the porous matrix; Eq. (5) states that at large distances from the borehole, the concentration is unchanged; and Eq. (6) states that the concentration in the formation at the borehole wall is equal to the concentration in the fluid column of the borehole.

The concentration in the borehole, C_{w}, is governed by the following balance equation for the mass of the chemical constituent in the borehole:

$$V\frac{dC_{\mathrm{w}}}{dt} = AnD\frac{\partial c}{\partial r}\bigg|_{r=R} \tag{7}$$

where A is the surface area of the borehole through which there is diffusion, V is the volume of the fluid in the borehole, and n is the porosity of the porous matrix. Equation (7) is subject to the following initial condition,

$$C_{\mathrm{w}}(t=0) = C_{\mathrm{B}} \tag{8}$$

where C_{B} is the initial concentration of the chemical constituent in the borehole.

To solve Eqs. (3)–(8), the following change in variables is applied,

$$c'(r,t) = c(r,t) - C_{\mathrm{m}} \tag{9}$$

$$C'_{\mathrm{w}} = C_{\mathrm{w}} - C_{\mathrm{m}} \tag{10}$$

and the resulting governing equations and boundary conditions are solved in the Laplace domain. Introducing Eqs. (9) and (10) into Eqs. (3)–(8) and taking the Laplace transformation yields

$$p\overline{c'} - D\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\overline{c'}}{\partial r}\right) = 0 \tag{11}$$

$$\overline{c'}(r\to\infty) = 0 \tag{12}$$

$$\overline{c'}(r=R) = \overline{C'_{\mathrm{w}}} \tag{13}$$

$$V\left(p\overline{C'_{\mathrm{w}}} - C_{\mathrm{B}} + C_{\mathrm{m}}\right) = AnD\frac{\partial\overline{c'}}{\partial r}\bigg|_{r=R} \tag{14}$$

where p is the Laplace transform variable, and $\overline{c'}$ and $\overline{C'_{w}}$ are the Laplace transforms of c' and C'_{w}, respectively.

The solution to Eq. (11) is

$$\overline{c'}(r) = \overline{C'_{\mathrm{w}}}\frac{K_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}r\right]}{K_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]} \tag{15}$$

where the boundary conditions given in Eqs. (12) and (13) have been applied, and K_0 is the modified Bessel function of the second kind of order 0. Eq. (15) is introduced into Eq. (14) to solve for $\overline{C_{\mathrm{w}}{}'}$,

$$\overline{C_{\mathrm{w}}{}'} = \frac{V(C_{\mathrm{B}} - C_{\mathrm{m}})K_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]}{pVK_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right] + An(Dp)^{\frac{1}{2}}K_1\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]} \tag{16}$$

which in turn is introduced into Eq. (15) to yield the Laplace transform solution for the concentration in the formation at any radial distance from the borehole,

$$\overline{c'}(r) = \frac{V(C_{\mathrm{B}} - C_{\mathrm{m}})K_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}r\right]}{pVK_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right] + An(Dp)^{\frac{1}{2}}K_1\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]} \tag{17}$$

The Laplace transform for $\overline{C_{\mathrm{w}}}$ and $\overline{c}$, rather than $\overline{C_{\mathrm{w}}{}'}$ and $\overline{c'}$, are obtained by taking the Laplace transform of Eqs. (9) and (10) and introducing the results into the above equations to yield

$$\overline{C_{\mathrm{w}}} = \frac{C_{\mathrm{m}}}{p} + \frac{V(C_{\mathrm{B}} - C_{\mathrm{m}})K_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]}{pVK_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right] + An(Dp)^{\frac{1}{2}}K_1\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]} \tag{18}$$

$$\overline{c}(r) = \frac{C_{\mathrm{m}}}{p} + \frac{V(C_{\mathrm{B}} - C_{\mathrm{m}})K_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}r\right]}{pVK_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right] + An(Dp)^{\frac{1}{2}}K_1\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]} \tag{19}$$

From Eq. (19), the mass flux entering or leaving the borehole can also be calculated. The mass flux into or out of the borehole at a given time is defined by Eq. (7). Integrating Eq. (7) over time yields the total mass flux into or out of the borehole during the experiment,

$$F(t) = \int_{\tau=0}^{\tau=t}\left(AnD\frac{\partial c(\tau)}{\partial r}\bigg|_{r=R}\right)d\tau \tag{20}$$

where F is the total mass into or out of the borehole from the start of the test to time t. Taking the Laplace transformation of Eq. (20) yields

$$\overline{F} = AnD\frac{1}{p}\frac{\partial \overline{c}}{\partial r}\bigg|_{r=R} \tag{21}$$

where $\overline{F}$ is the Laplace transformation of F at time t. Introducing Eq. (19) into Eq. (21) yields

$$\overline{F} = -\frac{AnV(C_{\mathrm{B}} - C_{\mathrm{m}})K_1\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]}{\left(\frac{p}{D}\right)^{\frac{1}{2}}pVK_0\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right] + pAnK_1\left[\left(\frac{p}{D}\right)^{\frac{1}{2}}R\right]} \tag{22}$$

The solutions for C_{w}, c, and F are obtained by performing the inverse Laplace transformation to Eqs. (18), (19), and (22), respectively. A numerical algorithm for performing the inversion of the Laplace transformation solution was implemented (see, e.g., Crump 1976) to identify $C_{\mathrm{w}}(t)$, $c(t)$, and $F(t)$.

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