DT# 46987 QA:NA 6/20/06 CB

Scale Dependence of the Effective Matrix Diffusion Coefficient: Evidence and Preliminary Interpretation

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1. Introduction

The exchange of solute mass (through molecular diffusion) between fluid in fractures and fluid in the rock matrix is called matrix diffusion. Owing to the orders-of-magnitude slower flow velocity in the matrix compared to fractures, matrix diffusion can significantly retard solute transport in fractured rock, and therefore is an important process for a variety of problems, including remediation of subsurface contamination and geological disposal of nuclear waste. The effective matrix diffusion coefficient (molecular diffusion coefficient in free water multiplied by matrix tortuosity) is an important parameter for describing matrix diffusion, and in many cases largely determines overall solute transport behavior. While matrix diffusion coefficient values measured from small rock samples in the laboratory are generally used for modeling field-scale solute transport in fractured rock (Boving and Grathwohl, 2001), several research groups recently have independently found that effective matrix diffusion coefficients much larger than laboratory measurements are needed to match field-scale tracer-test data (Neretnieks, 2002; Becker and Shapiro, 2000; Shapiro, 2001; Liu et al., 2003, 2004a).

In addition to the observed enhancement, Liu et al. (2004b), based on a relatively small number of field-test results, reported that the effective matrix diffusion coefficient might be scale dependent, and, like permeability and dispersivity, it seems to increases with test scale. This scale-dependence has important implications for large-scale solute transport in fractured rock. Although a number of mechanisms have been proposed to explain the enhancement of the effective matrix diffusion coefficient, the potential scale dependence and its mechanisms are not fully investigated at this stage. The major objective of this study is to again demonstrate (based on more data published in the literature than those used in Liu et al. [2004b]) the potential scale dependence of the effective matrix-diffusion coefficient, and to develop a preliminary explanation for this scale-dependent behavior.

2. Work Description

2.1 *Literature survey of effective matrix diffusion coefficient*

A relatively comprehensive literature survey of field tracer tests and the corresponding effective diffusion coefficient values was conducted. Forty field tracer tests at 15 fractured geologic sites were selected for this study, based on data availability and quality.

Four major criteria are used for selecting the tracer tests used in this study. First, the selected tracer tests must be conducted in fractured rock with a significant contrast between fracture and matrix permeability. Tracer tests conducted in other fractured porous media were not considered here. Second, the tracers used in the selected tests must be conservative. For nonconservative tracers, one or more additional parameters are needed to account for the corresponding adsorptive, reactive, or radioactive decay processes, complicating the transport-parameter calibration. Third, a selected tracer test must be well defined, with clear breakthrough curves and sufficient test details published (e.g., injection mass, injection and pumping rates), so that meaningful simulations can be performed. These data are critical for accurate calibration of the transport parameters using the analytic models. Finally, the necessary fracture and matrix properties must be available for calculating the effective matrix diffusion coefficient.

For the field tracer tests without reported matrix-diffusion coefficient values, reanalysis of the tracer breakthrough curves was needed to calibrate transport parameters that included the effective matrix diffusion coefficient. This reanalysis was conducted using an analytic solution for linear flow and a semi-analytic solution for radial flow in fractured rock systems (Maloszewski and Zuber, 1985, 1990; Reimus et al., 2003). These analytic solutions and similar solutions (e.g., Tang et al., 1981; Sudicky and Frind, 1982) have been used for calibrating the matrix diffusion coefficient values reported in the literature.

To investigate the possible scale dependence of the effective matrix diffusion coefficient, we employ the effective-matrix-diffusion-coefficient factor, F_d, which is defined as the ratio of the effective matrix diffusion coefficient (D_m^e) to the lab-scale matrix diffusion coefficient (D_m):

$$F_d = \frac{D_m^e}{D_m}. \tag{1}$$

The lab-scale matrix diffusion coefficient (D_m) used in Equation (1) is the mean value of laboratory measurements for small rock-matrix samples from the same geologic site. When such measurements are not available, Archie's law (Boving and Grathwohl, 2001) is used to approximate this value, based on

$$D_m = \phi_m^{n-1} D_w , \tag{2}$$

where D_w is the molecular diffusion coefficient of a tracer in free water, ϕ_m is matrix porosity, and n is an empirical parameter, which is generally larger than 2.0. To avoid potential exaggeration of scale effects (or an artificial increase in estimated F_d values), we used $n = 2$ here. Unlike the effective matrix diffusion coefficient, F_d is expected to be independent of individual tracers used in field tests, but would depend on the scaling effects of fractured rock characteristics. In the survey, the effective matrix diffusion coefficient and its factor are calculated for each tracer test.

2.2 *A preliminary interpretation*

Water flow and solute transport processes in fractured rock are complicated by the involved heterogeneity at different scales and the complex geometry of fracture networks. Although different conceptual models for flow and transport in fractured rock exist, many studies indicate that a flow pattern is mainly characterized by many flow channels (or separated individual flow paths) (e.g., Tsang and Neretnieks, 1998). Different channels or paths have different flow and transport properties, resulting in large-scale heterogeneities. In this study, we focus on mass transfer among sub-fractures and the surrounding rock matrix associated with a single major flow path, as illustrated in Figure 1 using an idealized, but rather general, sub-fracture geometry. As demonstrated later, understanding this mass-transfer process may hold the key to understanding why the effective matrix diffusion coefficient is scale-dependent.

Water flow in a single flow path (or main channel) has been often simplified as a flow process within a single straight fracture (e.g., Neretnieks, 2002; Becker and Shapiro, 2003). In reality, however, flow structure is more complicated than that, owing to the complexity of fracture-network geometry. Percolation models (that study network connectivity and characteristics of cluster structures) provide a more realistic representation of flow-path geometry (e.g., Stauffer and Aharony, 1994; Renshaw, 1999). We use the percolation theory herein to characterize the geometry of a flow path in a fracture network for our numerical experiments.

Based on the percolation theory, the geometry of a main flow path (backbone) has several useful features. First, not all the fractures in a flow path are singly connected. The singly connected segments are often separated by structures that contain several routes in parallel that are called *loops*. Second, it is well known that percolation structures at percolation threshold (or at scales less than a correlation length) exhibit fractal-like scaling properties. Third, the above two features were originally observed for networks consisting of randomly distributed bonds with the same lengths. Networks of this kind are investigated in the classic application of percolation theory. However, because of heterogeneity, real-world fracture networks are generally more complicated. It is well documented that the trace length distribution of fractures follows a power law, and longer fractures generally have larger apertures. In this case, the two features mentioned above are still valid with additional complications.

Numerical experiments were designed to investigate solute transport processes through a flow path in a fracture network, with a focus on the effective matrix diffusion coefficient as a function of travel distance from the source. The flow paths were constructed to be consistent with the features discussed above.

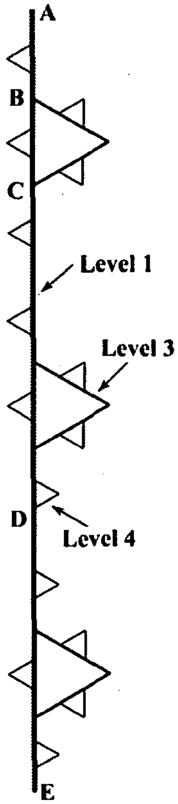

Figure 1. An idealized flow path constructed based on percolation theory. The tracer source is located at location A and breakthrough curves are monitored at locations B, C, D and E.

Figure 1 shows a flow path constructed using a deterministic recursive procedure. The Level 1 fracture in Figure 1 represents connected long fractures that form singly connected segments in a network and a major conduit at locations where multiple loops exist. Higher-level fractures (with a shorter trace length and smaller fracture aperture than Level 1) are then added, and an equilateral triangle is formed where the loop occurs.

Once a steady-state flow field was established in the flow path (Figure 1), tracer was released from point A (with a constant tracer concentration), and breakthrough curves at points B, C, D and E are simulated. The tracer transport simulation was based on a particle-tracking approach applicable to fracture flow that is available in the literature (Painter et al., 2005; Cvetkovic, 2003). The effective parameters (including effective matrix diffusion coefficient) are determined by fitting the numerical experiment results (breakthrough curves at different locations) to the analytical solution for solute transport along a single fracture (Zhou, 2005). A similar curve-fitting approach has often been used in interpreting field-scale tracer testing results.

3. Results and Discussion

Figure 2 shows the literature-survey results for the effective matrix diffusion coefficient. In this figure, F_d refers to the ratio of observed effective matrix diffusion coefficient to the lab-scale value. The three big points correspond to average values at lab scale, a scale on the order of tens of meters, and a scale on the order of hundreds of meters, respectively. Note that the big point corresponding to the lab scale actually represents many data points with identical F_d values. Any data point in the other two groups has a data point corresponding to the lab scale. Although a high degree of fluctuation exists, the ratio, on average, is scale dependent and generally increases with test scale.

In addition to the effective matrix diffusion coefficient, we also collected or estimated longitudinal dispersivity values for different tracer tests. To evaluate the reasonableness of our calibrated transport parameters, we checked the consistency of the dispersivity data in this study with past studies of calibrated dispersivity versus scale. As indicated in Figure 3, our dispersivity data are within the range of a well-known literature survey results of large-scale dispersivity reported by Gelhar et al. (1992).

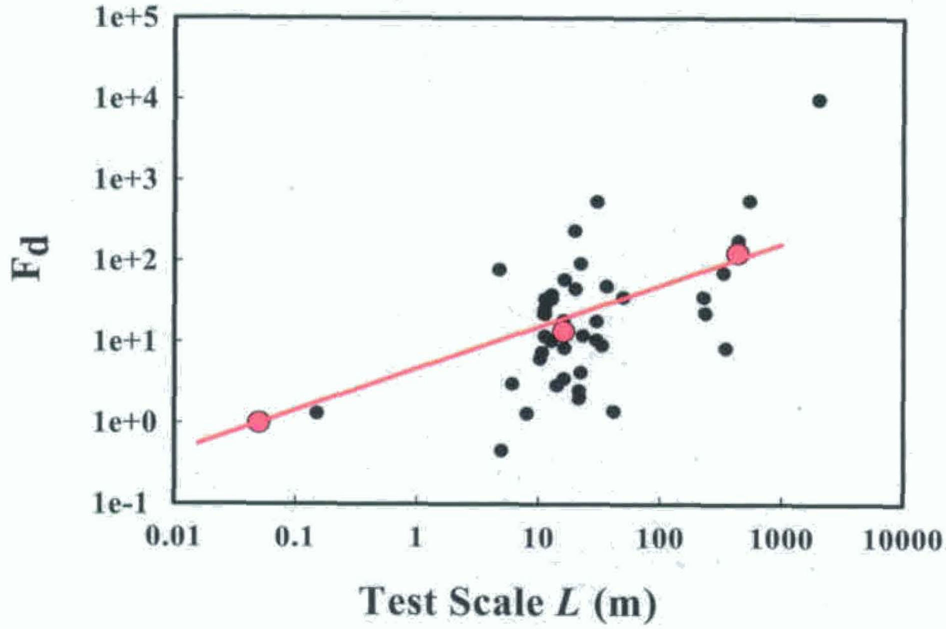

Figure 2. The ratio of observed effective matrix diffusion coefficient to the lab-scale value (F_d) as a function of test scale. The three enlarged points correspond to average values at the lab scale, a scale on the order of tens of meters, and a scale on the order of hundreds of meters, respectively.

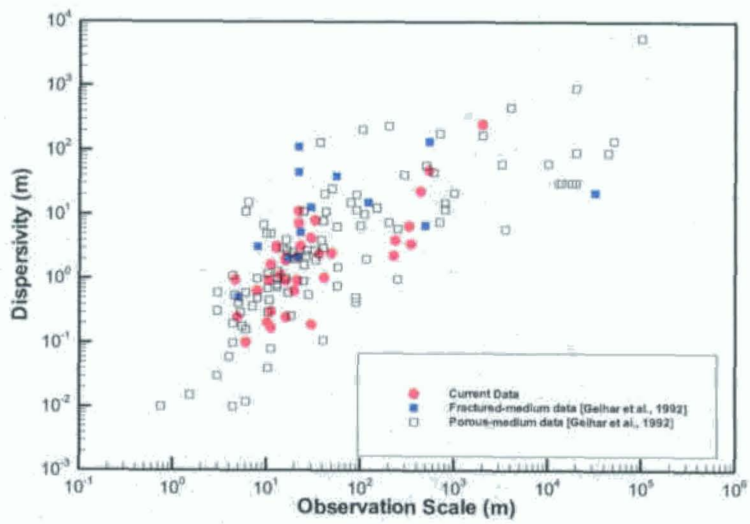

Figure 3. Comparison of the field-scale longitudinal dispersivity between the current study for fractured rock and a previous study for both porous and fracture media [*Gelhar et al.*, 1992]

As previously indicated, numerical experiments were performed to explore the mechanisms behind the potential scale dependence of the effective matrix diffusion coefficient. Figure 4 shows the calibrated (normalized) effective matrix diffusion coefficient as a function of distance (from a location where the breakthrough curve is simulated to the fixed location where a tracer is initially released) for the flow path shown in Figure 1. Obviously, the effective matrix diffusion coefficient is indeed dependent on the travel distance, which is consistent with the literature survey results. Note that numerical experiments provide a useful alternative way to better support or refute potential scale-dependent behavior, because they can be conducted under well-controlled conditions and interpreted in an unambiguous manner.

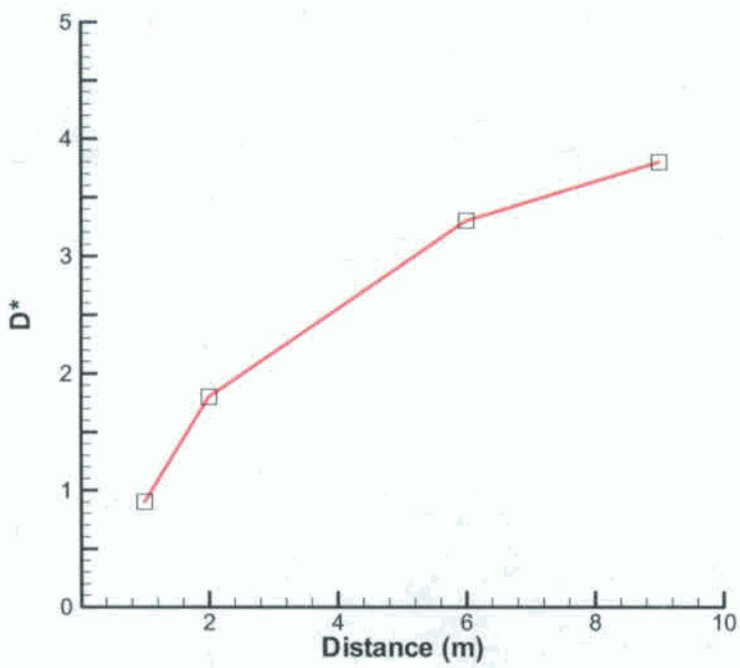

Figure 4. Fitted relative effective-matrix-diffusion coefficient values (D*) as a function of distance for a flow path consisting of flow loops as illustrated in Figure 1.

The current numerical experiments also indicate that a combination of the local flow loops and the associated matrix diffusion process, together with scaling properties in the flow-path geometry, seems to be the major mechanism (at a range of scales) for the observed scale dependence of the effective matrix diffusion coefficient (Figure 5), while other potentially important mechanisms may still exist and need to be investigated in future studies.

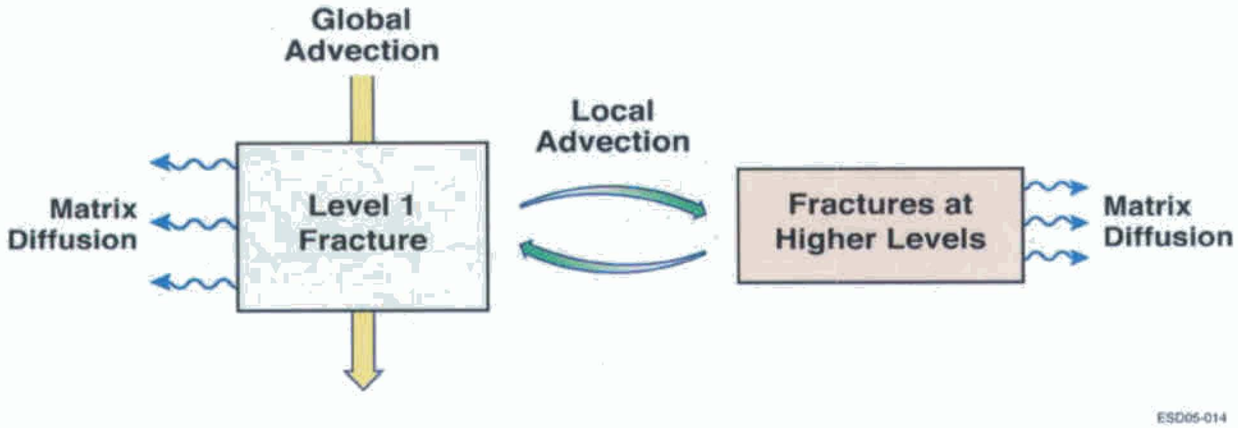

Figure 5. A conceptual diagram illustrating effective matrix diffusion as a combination of local-scale advection and matrix diffusion in fractures at different scales.

4. Conclusion

A relatively comprehensive literature survey and the results of numerical experiment demonstrate that the effective matrix-diffusion coefficient, like permeability and dispersivity, is scale-dependent and increases with test scale. A combination of local flow loops and the associated matrix diffusion process, together with scaling properties in flow-path geometry, seems to be the major mechanism (at a range of scales) for the observed scale dependence of the effective matrix diffusion coefficient. This finding has many important implications for problems involving matrix diffusion.

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