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Tracer transport in fractured crystalline rock: Evidence of nondiffusive breakthrough tailing

Matthew W. Becker
Department of Geology, State University of New York at Buffalo

Allen M. Shapiro
U.S. Geological Survey, Reston, Virginia

Abstract. Extended tailing of tracer breakthrough is often observed in pulse injection tracer tests conducted in fractured geologic media. This behavior has been attributed to diffusive exchange of tracer between mobile fluids traveling through channels in fractures and relatively stagnant fluid between fluid channels, along fracture walls, or within the bulk matrix. We present a field example where tracer breakthrough tailing apparently results from nondiffusive transport. Tracer tests were conducted in a fractured crystalline rock using both a convergent and weak dipole injection and pumping scheme. Deuterated water, bromide, and pentafluorobenzoic acid were selected as tracers for their wide range in molecular diffusivity. The late time behavior of the normalized breakthrough curves were consistent for all tracers, even when the pumping rate was changed. The lack of separation between tracers of varying diffusivity indicates that strong breakthrough tailing in fractured geologic media may be caused by advective transport processes. This finding has implications for the interpretation of tracer tests designed to measure matrix diffusion in situ and the prediction of contaminant transport in fractured rock.

1. Introduction

Pulse injection tracer tests conducted in fractured rocks typically result in a recovered concentration history (breakthrough) that is highly skewed to later times, particularly when compared to advection and dispersion in unconsolidated porous media. The most common explanation for this "breakthrough tailing" is that while some of the tracer moves quickly through open channels, a significant fraction of the tracer is delayed by diffusive exchange with the rock matrix. Tracer mass that moves primarily through open channels results in an early peak in concentration, while the tracer that is heavily influenced by diffusive exchange results in a low concentration "tail" over an extended period of time. The exchange of mass between relatively mobile fluid in the fracture and relatively immobile fluid in the rock matrix is usually called "matrix diffusion."

The matrix diffusion concept of transport in fractured geologic media has been the basis of numerous mathematical models. The most widely used model involves advective and dispersive transport in the fracture coupled to diffusive transport into the porous matrix [*Tang et al.*, 1981; *Maloszewski and Zuber*, 1985; *Moench*, 1995]. This model and its successors have been used successfully to fit a number of field tracer tests in fractured rock [e.g., *Maloszewski and Zuber*, 1993; *Moench*, 1995]. In fact, these models have achieved such acceptance that it has been suggested that an extended breakthrough tail indicates that matrix diffusion has influenced transport [*Tsang*, 1995; *Meigs et al.*, 1996].

Several variations on the matrix diffusion concept have been hypothesized. While most researchers have proposed that molecular diffusion of tracer into the porous matrix explains breakthrough tailing [*Grisak et al.*, 1980; *Neretnieks*, 1980; *Neretnieks et al.*, 1982; *Birgersson et al.*, 1993; *Maloszewski and Zuber*, 1993; *Novakowski and Lapcevic*, 1994; *Moench*, 1995; *Novakowski et al.*, 1995; *Sanford et al.*, 1996], others have conjectured that diffusion into interchannel small-aperture spaces in the fracture itself serves as a diffusive sink for mass in the fractures [*Rasmuson and Neretnieks*, 1986; *Abelin et al.*, 1991, 1994; *Johns and Roberts*, 1991; *Dykhuizen*, 1992]. Still others have proposed models by which mass is exchanged with stagnant fluid along the fractures walls [*Coats and Smith*, 1964; *Raven et al.*, 1988] or by diffusion into an unspecified distribution of stagnant fluids associated with the fracture and matrix [*Haggerty and Gorelick*, 1995; *Haggerty et al.*, 1999].

In spite of the abundance of theoretical explanations of breakthrough tailing, direct evidence of diffusion-influenced transport is rare. *Jardine et al.* [1999] conducted natural gradient tracer tests in a fractured saprolite and measured concentrations of tracer in both the matrix and fracture. They found good agreement between model-predicted and measured tracer concentration in the matrix, giving a clear indication that matrix diffusion can, indeed, influence tracer breakthrough from long-term tracer experiments conducted in fractured permeable rock. Recently, *Dijk et al.* [1999] used magnetic resonance imaging to find relatively stagnant fluid along the walls of a fractured limestone sample, but they did not investigate the influence of this fluid on solute transport.

In lieu of direct evidence of matrix diffusion, the most compelling argument for diffusion-influenced breakthrough tailing comes from field tests employing multiple tracers with varying rates of molecular diffusion [*Jardine et al.*, 1999]. A separation in the breakthrough curves produced by solute tracers of different diffusivity suggests that transport is in some way dependent upon molecular diffusion. *Garnier et al.* [1985] conducted

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field experiments in a fractured chalk using fluorescein, iodide, and deuterium as tracers. A clear separation in the three breakthrough curves was observed and was later explained using a matrix diffusion model [*Maloszewski and Zuber*, 1990; *Moench*, 1995]. *Sanford et al.* [1996] observed similar breakthrough separation of gas tracers in a fractured saprolite.

Another approach to detecting matrix diffusion is to use both solute and colloid tracers. In this type of experiment, breakthrough separation might indicate that solutes diffused into the matrix, while colloids were excluded on the basis of their size. Such experiments have been attempted in consolidated and unconsolidated fractured media, but quantitative analysis has been hampered by the typically low recovery of the colloid [e.g., *McKay et al*., 1993; *Reimus et al*., 1998; *Becker et al*., 1999].

To date, therefore, the most commonly cited field evidence of matrix diffusion is an extended tail on a single tracer breakthrough curve [e.g., *Grisak et al*., 1980; *Neretnieks et al*., 1982; *Birgersson et al*., 1993; *Maloszewski and Zuber*, 1993; *Novakowski and Lapcevic*, 1994; *Novakowski et al*., 1995; *Meigs et al*., 1996]. Because this interpretation requires the simultaneous fitting of at least three parameters (one each for advection, dispersion, and diffusion), the relative influence of advection, hydrodynamic dispersion, and matrix diffusion on the breakthrough tail cannot be known with certainty. Given the additional complication that none of these three transport processes are clearly understood in fractured media [*National Research Council*, 1996], without corroborating evidence it would seem premature to conclude that matrix diffusion influences transport in a fractured system based on the breakthrough tailing of a single tracer.

This article discusses field tracer tests that resulted in breakthrough curves exhibiting strong tailing that cannot be explained by diffusive mass exchange. Diffusive transport is constrained by using tracers of varying molecular diffusivity and by repeating the tests at different transport velocities (pumping rates). To assure that tailing was not an artifact of the injection method, tracer was continuously mixed with water in the injection borehole, and the tracer concentration was monitored throughout the injection process. In addition, both a weak dipole and convergent test design were used. On the basis of our interpretations, diffusive exchange with both the rock matrix and stagnant water in fractures is ruled out, and we must conclude that advective processes were responsible for the significant breakthrough tailing that was observed. This result indicates that commonly used conceptual and mathematical models of mass transport that are suitable for other fractured systems are not necessarily appropriate for fractured crystalline rocks.

2. Site Description and Hydrogeology

Tracer tests were conducted in the bedrock of the Hubbard Brook Experimental Forest in the southern part of the White Mountains in Grafton County, New Hampshire (Figure 1). This site, which is maintained by the U.S. Forest Service, has been a focal point of U.S. Geological Survey research in fractured rock terrain where field techniques and interpretive methods have been developed to better understand groundwater flow and contaminant transport in fractured crystalline bedrock [*Shapiro and Hsieh*, 1991]. The tests described in this article were conducted in the Forest Service East (FSE) well field (Figure 1, insert) [*Shapiro and Hsieh*, 1996a, 1996b].

The local bedrock is typified by pelitic schist that has been metamorphosed to a sillimanite grade and is extensively intruded by dikes, anastomosing fingers, and pods of granite [*Barton*, 1996]. The granite appears to be more densely fractured than the schist, and although both the granite and schist are crosscut by pegmatite and aplite dikes, fractures are not typically associated with these later intrusions (C. D. Johnson, personal communication, 1997). Bedrock in the vicinity of the FSE well field is overlain by glacial drift that is 18–24 m in depth.

The FSE well field consists of 14 bedrock boreholes that range in depth from 60 to 230 m. Bedrock boreholes are 15 cm in diameter and are cased through the glacial drift and 3 m into the bedrock. The groundwater in many of the bedrock wells in the FSE well field tends to be reducing, possibly because of septic system discharges in the overburden. Water samples taken during pumping for the tracer tests had a pH of ~6. *Tiedeman et al*. [1998] provide further discussion of the groundwater hydrology of the Mirror Lake basin.

Pumping tests, single-hole fluid injection tests, cross-hole hydraulic tests, and slug tests were used to determine the hydraulic conductivity along the length of bedrock boreholes, hydraulic connections between boreholes, and transmissivity of formation of fractures [*Hsieh and Shapiro*, 1996; *Shapiro and Hsieh*, 1998]. These data have led to a conceptual model of the spatial distribution of the hydraulic conductivity. Within the FSE well field, which covers an area of $\sim 120 \times 120$ m, there are several zones of highly conductive fractures. These zones tend to be constrained spatially over distances of tens of meters and are not necessarily hydraulically connected to one another. During hydraulic tests, therefore, wells had to be equipped with packers to preserve the natural hydraulic structure of the formation.

Standard geophysical logging tools, an acoustic televiewer, and a submersible borehole television camera have been used to determine rock type and the location and orientation of fractures in the boreholes of the FSE well field [*Johnson and Dunstan*, 1998]. These data indicate that the conductive fractures isolated in the pumping well, FSE6, are both steeply dipping and horizontal. The single conductive fracture isolated in the injection well, FSE9, was observed to be near horizontal. Because FSE6 and FSE9 are separated by a distance of 36 m and fractures exposed in nearby road cuts rarely exceed 10 m in length [*Barton et al*., 1997], it is unlikely that the two wells are connected by a single fracture. The orientation and relationship of the fractures that hydraulically connect the two wells is unknown, but on the basis of outcrop observations it is expected to be very complex.

Studies of the matrix properties of the bedrock near Mirror Lake were conducted on small granite and schist blocks taken from road cuts [*Wood et al*., 1996]. The weight-derived average porosity for granite and schist was found to be 1.46 and 1.87%, respectively. After saturating the blocks over a period of 6 months, diffusion studies were carried out by immersing the blocks in a solution of ^{137}Cs and grinding away successive layers of the rock to gauge the penetration depth. The effective diffusion coefficient of ^{137}Cs in granite was found to 6×10^{-9} cm^2/s.

Although ^{137}Cs is expected to be retarded in its transport with respect to nonreactive tracers, *Skagius and Neretnieks* [1988] found that ^{137}Cs and iodide had rates of diffusion within an order of magnitude of one another. The matrix diffusion rate determined from ^{137}Cs migration is therefore considered

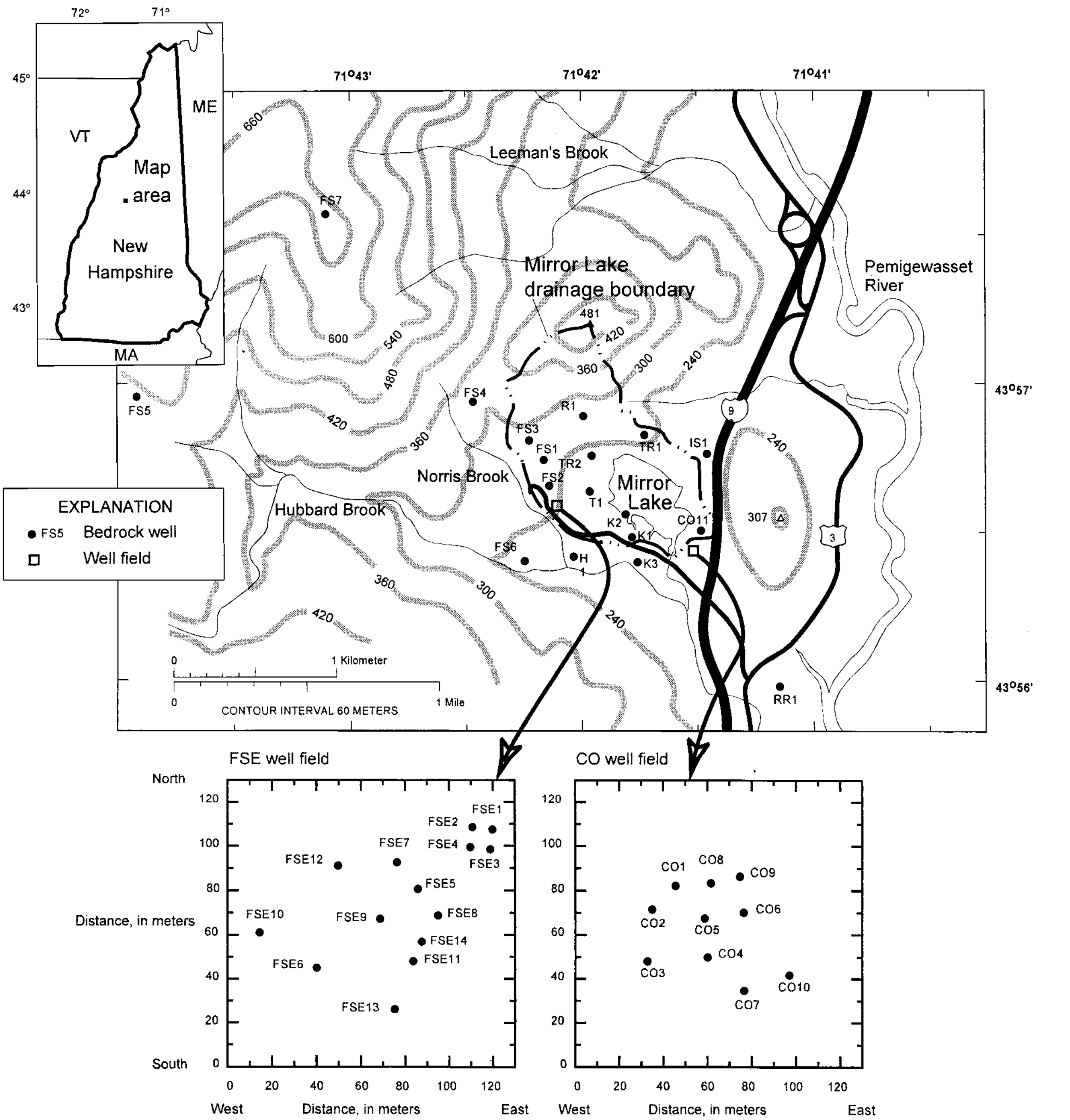

Figure 1. Location of the test site. Tracer tests were conducted in the FSE well field in the Hubbard Brook Experimental Forest, Grafton County, New Hampshire.

to be a reasonable approximation of the diffusion rate expected for bromide, which has a diffusion rate in water near that of iodide. Additional studies have found diffusion rates of conservative tracers in crystalline rock of the order of 10^{-10}–10^{-9} cm^2/s [*Skagius and Neretnieks*, 1986; *Birgersson and Neretnieks*, 1990]. For the purposes of these experiments, a value of 6×10^{-9} cm^2/s is assumed to be the order-of-magnitude estimate of the rate of bromide diffusion into the rock matrix.

3. Experimental Method

The tracers used for these experiments were selected because they were considered (1) to be nontoxic, (2) to be nonreactive with immobile subsurface material, (3) to be detectable at low concentrations, (4) to have a density at injection concentrations near that of water, and (5) to have a wide range in molecular diffusivity. Gas tracers were rejected because the rate of sample collection necessary in a forced gradient experiment was not compatible with available sampling techniques [*Sanford et al.*, 1996]. Colloid tracers were used in these tests, but because <50% of the injected mass was recovered in all cases, they are considered elsewhere [*Becker et al.*, 1999]. The fluorescent dye, Lissamine FF, was also used in the first test performed in 1997 but was abandoned because it appeared to be partitioning strongly to the formation.

The tracers considered here are deuterated water (HDO,

Table 1. Rates of Molecular Diffusion in Water (at 25°C) of Some Tracers Used at Mirror Lake

Tracer	Free Diffusion Rate, cm^2/s	Source
HDO	2.3×10^{-5}	*Wang et al.* [1953]
Br^-	2.0×10^{-5}	*Sanford et al.* [1996]
PFBA	6.6×10^{-6}	*Reimus et al.* [1997]

HDO, deuterated water; PFBA, pentafluorobenzoic acid.

injected as D_2O, 99.9% pure), bromide (injected as NaBr), and pentafluorobenzoic acid (PFBA). These solutes are expected to be nonreactive with geologic material on the basis of previous laboratory and field experiments [*Moench*, 1995; *Becker*, 1996; *Sanford et al*., 1996; *Reimus et al*., 1997, 1998]. The diffusivity of the tracers in pure water at ~25°C were obtained from the literature and are listed in Table 1. An examination of Table 1 will show that the diffusivity of the tracers varies by a factor of ~3.5.

The tests were conducted in two field seasons, using two different forced gradient designs. In the summer of 1996, bromide tracer tests were conducted using a convergent design, which involved pumping well FSE6 and injecting a slug of tracer in well FSE9, 36 m away. The injection interval was defined by three inflatable packers: two outer packers to isolate the interval in the well bore and an inner packer to seal the fracture (as described by *Shapiro and Hsieh* [1996b]). While the center packer was inflated, the tracer was mixed in the injection interval by circulating fluid to and from the surface using a down-hole pump. Once a homogeneous injection fluid was achieved, the inner packer was deflated, allowing tracer to enter the formation under the weight of the fluid column to the surface. Reinflating the inner packer terminated the injection. By this method it could be assured that a finite slug of tracer (~10 L of a 16.9 g/L bromide solution injected at 3.3 L/min) left the well bore.

In the summer of 1997, tracer tests were performed between the same well pair, using a different configuration. The pumping rate in FSE6 was as in the convergent flow tests, but 5% of the pumped water was routed to the injection well, FSE9. This type of a hydraulic configuration is often referred to as a "weak dipole." With the two outer packers inflated, the injection zone of well FSE9 was constantly mixed and monitored by circulating fluid to a 5 L reservoir at the surface using a down-hole pump. Because this circulation flow rate was at least an order of magnitude larger than the injection flow rate, the approximate injection concentration could be measured continuously at the surface. Reinjection was accomplished by teeing a 0.635 cm diameter tube into the discharge line at the pumped well. A valve in the discharge line, down flow of the tee, provided enough backpressure to force water into the injection interval at the controlled flow rates indicated in Table 2. The pumping rate in FSE6 and the circulation and injection rate in FSE9 were monitored throughout the tests using flow meters calibrated volumetrically. Transducers in the injection zone and above and below the injection zone assured that the packers maintained a good seal in the well bore.

Injection for the weak dipole tests proceeded generally in the following manner. For several days prior to injection the well field was brought to a relatively steady state by running the weak dipole pumping and reinjection system. Immediately prior to injection, the center packer was inflated to seal the fracture, while reinjection was temporarily diverted. A cocktail containing known masses of dissolved tracer was then added to flow-through reservoir at the surface, and the circulating pump was allowed to mix the borehole fluids until a steady concentration was measured in the circulating fluid, usually after ~15 min. Subsequently, injection was initiated by deflating the center packer and simultaneously diverting the reinjection fluid back to the injection well. Weak dipole tests were repeated at four different pumping rates (see Table 2). Only in tests C and D was PFBA used as a tracer.

The weak dipole design was selected as the primary approach to investigating breakthrough tailing for a number of reasons. First, in a weak dipole experiment, tracer is injected into a pseudo steady state flow field, which was expected to minimize transient effects from injection that might be mistaken for matrix diffusion. Second, experience with convergent and weak dipole tests at another crystalline rock study site [*Becker*, 1996; *Becker and Charbeneau*, 2000] suggested that the weak dipole design minimized the influence of near-borehole hydraulic characteristics. For example, if the well was located in an anomalously tight area of the fracture, the tracer would still enter the formation in an efficient manner. Third, previous experience also indicated that tracer recovery might be improved under a weak dipole design. The 5% reinjection rate was chosen because it was the lowest rate that could be practically maintained by the available pumps and plumbing.

4. Experimental Results

Drawdown responses observed in the FSE well field during pumping of FSE6 were similar to those resulting from previous tests for corresponding pumping rates. While the five boreholes within 60 m of FSE6 showed immediate and significant drawdown, more distant wells had a delayed drawdown response to pumping and a less significant drawdown. Three-dimensional numerical flow modeling of the FSE well field suggests a transmissivity of the fractures connecting FSE6 and

Table 2. Pumping Rates, Injected Mass, and Percent Ultimate Recovery for the Convergent Flow and Weak Dipole Flow Tracer Tests Conducted at Mirror Lake

Test	*Q* FSE6, L/min	*Q* FSE9, L/min	Injected Mass, g			Mass Recovered, % (of Injected)		
			HDO	Br^-	PFBA	HDO	Br^-	PFBA
Conv	4.5	3.3 (slug)	0	169	0	···	83	···
A	8.3	0.42	59	100	0	104	103	···
B	5.2	0.22	60	100	0	99	99	···
C	2.9	0.14	80	100	40	89	92	92
D	9.8	0.48	98	100	55	94	99	98

Conv is convergent flow, and A, B, C, and D are the weak dipole tracer tests.

FSE9 of ~4.8 m^2/d [*Hsieh and Shapiro*, 1996a]. This transmissivity corresponds to a "cubic law" hydraulic aperture of ~400 μm [*Tsang*, 1992]. Transducer data from the closest wells also showed that the well field was in a near-steady state hydraulic condition when injection occurred in each of the tests. Measured background heads indicate that the natural hydraulic gradient was completely masked by the gradients induced by the pumping during the experiments.

In the weak dipole tests the concentration of tracer in the injection system decreased exponentially over time, as would be expected in a completely mixed system with constant and equal inflow and outflow [*Levenspiel*, 1972]. This exponentially decreasing trend was observed over a three-orders-of-magnitude change in concentration. In each test the residence time of tracer in the injection system was found to be <8% of the first moment of transport time in the formation, so that holdup of tracer in the well bore would be expected to have a relatively minor impact on tracer breakthrough. This expectation was confirmed using the transport model given in the appendix.

The injected mass and tracer recovery of the tests are given in Table 2. Note that the maximum theoretical recovery of tracer in the weak dipole tests is 105% because 5% of the pumped fluid was constantly reinjected. Tracer recovery appeared to decrease with decreasing weak dipole pumping and reinjection rate, and tracer recovery from the convergent test was poorer than all of the weak dipole tests. Figure 2 shows the breakthrough of bromide from all five tests plotted as concentration normalized to injected mass (C/M_0, where C is measured concentration and M_0 is the injected mass) versus the volume of water pumped from FSE6. Note that the tails of all breakthrough curves overlay one another when plotted in this manner.

Figures 3 and 4 display the breakthrough of all solute tracers from weak dipole tests C and D, respectively. Note that there is some separation of breakthrough of the different tracers at early time, exaggerated by the logarithmic abscissa, but at late time the breakthrough curves are indistinguishable from one another. Tests A and B also produced tracer breakthrough curves that essentially overlay one another within experimental error.

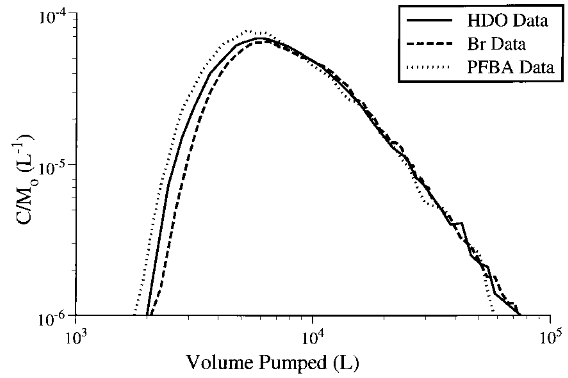

Figure 3. Normalized breakthrough of all tracers for test C (Q = 2.9 L/min).

5. Interpretation of Data

As discussed in section 1, a number of explanations have been proposed for the tailing of tracer breakthrough in fractured geologic media. In this section, we consider whether breakthrough tailing observed in tests conducted at the Mirror Lake site may have been caused by (1) an artifact of the tracer injection process, (2) fractional breakthrough of streamlines due to injection, (3) diffusive exchange of tracer with the rock, (4) diffusive exchange of tracer with stagnant water in the fracture, or (5) advective and hydrodynamic processes.

5.1. Artifacts of the Tracer Injection Process

The fact that the late time breakthrough for the convergent and weak dipole tests are similar regardless of injection design (Figure 2) implies that breakthrough tailing is not an artifact of injection. Because tracer concentration was mixed and measured in the injection borehole, it is clear that tracer holdup in the injection system, in particular, could not have caused the observed breakthrough tails.

There is a clear discrepancy in the early time breakthrough of convergent and weak dipole designs and among weak dipole experiments conducted at different pumping rates. It would appear that changes in the way tracer is injected can affect early time and peak breakthrough but does not significantly influence the late time arrival of tracer. The difference in the breakthrough curves at early time is a subject of ongoing investigation. It is possible, for example, that buoyancy-induced transport affected the early breakthrough but not the late

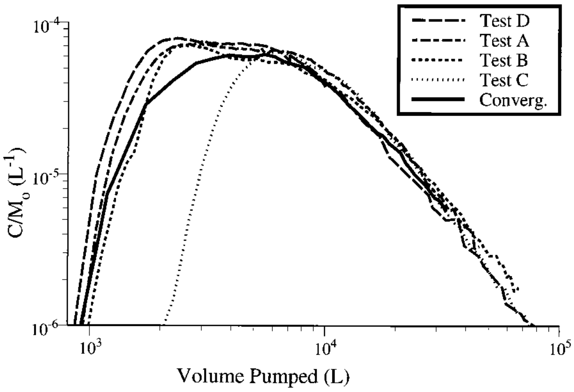

Figure 2. Normalized bromide breakthrough at pumping well for tests conducted between 1996 and 1997 in the bedrock near Mirror Lake.

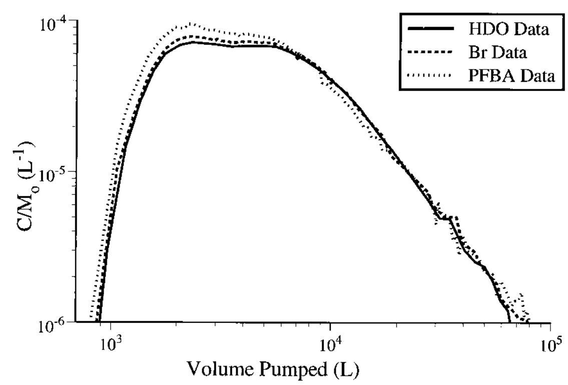

Figure 4. Normalized breakthrough of all tracers for test D (Q = 9.8 L/min).

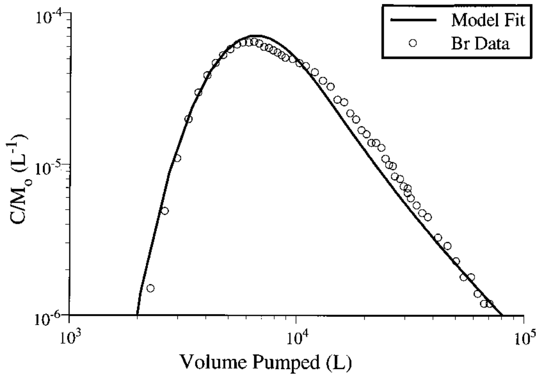

Figure 5. Fit of matrix diffusion model, given in the appendix, to the test C bromide breakthrough. The characteristic time of diffusion in the matrix (τ_p = 1480 min) is based on the free diffusion rate of bromide in water, and the residence time in the borehole (τ_s = 546 min) was measured. Fitted model parameters are Pe = 15 and τ = 1620 min.

breakthrough where the tracer solution was more diluted. The difference in the density of the injection fluids and the ambient groundwater was estimated to be between 0.01 and 0.02 g/cm^3 at the injection well, which is expected to result in buoyancy-induced transport in porous media [*Ronen et al.*, 1995; *Istok and Humphrey*, 1995]. To our knowledge, however, the effect of tracer solution buoyancy on tracer tests in fractured media has not been investigated.

5.2. Fractional Breakthrough of Streamlines

It is well-documented that tracer tests conducted in porous media using a full dipole hydraulic configuration (where injection and pumping rates are equal or nearly equal) can exhibit an extended breakthrough tail owing to an incremental arrival of tracers via streamlines of widely varying length [*Rainwater et al.*, 1987; *Welty and Gelhar*, 1994]. The tracer mass is divided at the injection well along the diverging streamlines, which ultimately terminate at the pumping well. Streamlines are of varying length, so that each parcel of tracer arrives at the withdrawal well at a different time, leading to an apparent dispersion of breakthrough at the withdrawal well. A similar result might be expected from dipole experiments conducted in fractured rock, although there have been no published studies of such experiments. In a weak dipole situation, where the injection flow rate is reduced, the effect of streamline divergence will be minimized but not removed.

We contend that the streamline divergence at the injection well was not a major influence on breakthrough tailing in these experiments on the basis of the fact that changing the test design from convergent to weak dipole did not appreciably change the measured breakthrough tail. Unfortunately, thus far we have been unable to confirm this contention theoretically. Two-dimensional numerical transport simulations in correlated random hydraulic conductivity fields were performed to model the influence of streamline divergence in a slug injection and constant injection two-well test. These simulations were inconclusive, however, primarily because the highly heterogeneous hydraulic conductivity variation that has been measured at Mirror Lake [*Shapiro and Hsieh*, 1998] could not be handled by numerical methods. Attempts to simulate tracer transport at the site continue.

5.3. Diffusive Exchange of Tracer With Rock

Matrix diffusion is often cited as the cause of tracer breakthrough tailing observed in fractured geologic media. Given the limited duration of the tracer tests at Mirror Lake and the <2% porosity of the rock matrix, it was not expected that a significant amount of tracer would diffuse out of the fractures. Nevertheless, some authors have used matrix diffusion to explain tailing observed in fractured crystalline rock [*Neretnieks et al.*, 1982; *Maloszewski and Zuber*, 1993], so the possibility of matrix diffusion is treated here.

The relationship between matrix diffusion and tracer breakthrough tailing depends on the relative rates of advection and hydrodynamic dispersion in the fracture and diffusion into the matrix. Consequently, it was necessary to apply a mathematical interpretation of the influence of matrix diffusion on tracer breakthrough at Mirror Lake. To keep the analysis simple and brief, a linear one-dimensional semianalytic mathematical model was employed that accounts for reinjection of the tracer and additional residence time in the injection borehole [*Becker and Charbeneau*, 2000]. The reader is referred to the appendix for a synopsis of the transport model.

The model was fit to weak dipole test C because it was carried out over the longest period of time and therefore had the greatest potential to be affected by matrix diffusion. Model parameters were based on the investigations discussed in section 2. Laboratory measurements of the granite matrix [*Wood et al.*, 1996] indicated that matrix porosity n_p should be set to 1.5% and the effective rate of molecular diffusivity D_p should be set to 6×10^{-9} cm^2/s. The effective tracer aperture, $2b$, was assumed to be 400 μm on the basis of the cubic law and a transmissivity of 4.8 m^2/d. Hydraulic apertures are considered to be indicators of effective apertures for tracers within an order of magnitude [*Tsang*, 1992].

Given these parameters, a reasonable fit of the test C bromide breakthrough could not be obtained by varying mean tracer travel time τ and the Peclet number Pe. In all cases, the tailing in the data was much more pronounced than the tailing produced by the model. In fact, the data could not be fit even when the matrix diffusion rate D_p was increased by 3 orders of magnitude over the expected rate (6×10^{-9} cm^2/s). We conclude therefore that the so-called matrix diffusion transport model cannot explain the magnitude of breakthrough tailing observed in these tests.

It is interesting to note that a reasonable fit of the test C breakthrough data could be obtained if the characteristic time of transport in the matrix τ_p was based on the diffusion rate in free water, which is over 3 orders of magnitude than that expected in the rock matrix. Figure 5 shows the result of assuming a τ_p based on the diffusion rate of bromide in free water ($D_p = 2 \times 10^{-5}$ cm^2/s) and manipulating Pe and τ until the best fit was achieved. The residence time of the tracer in the injection borehole τ_s was measured to be 564 min, so that the parameters of the best fit shown in Figure 5 are Pe = 15, τ = 1620 min, τ_p = 1480 min, and τ_s = 564 min. This result suggests that diffusion of bromide into stagnant water in the fracture itself might explain the observed bromide breakthrough tailing.

5.4. Diffusive Exchange of Tracer With Stagnant Water in Fractures

Although the transport model fit of the bromide data suggests that tracer diffused into immobile water in fractures, the data set as a whole does not support this conclusion. If the breakthrough tail was caused by diffusion of tracer into stagnant fluid in the fracture, we would expect to see a separation of breakthrough curves for tracers with differing rates of molecular diffusion in free water. For example, in a fractured chalk a clear separation of breakthrough was noted by *Garnier et al.* [1985] for the tracers fluorescein, iodide, and HDO, which have a similar range of molecular diffusivity as the tracers used in these experiments.

The breakthrough separation expected from the tracer exchange with stagnant fluid in the fractures at Mirror Lake can be estimated using the transport model given in the appendix. For this analysis, it is assumed that diffusive exchange is with water in the fracture itself, so that the rate of diffusion is equivalent to the rate of diffusion in free water (matrix porosity $n_p = 1$, and tortuosity equals 1). The differing rates of tracer molecular diffusion will result in a scaling of the characteristic time of diffusive transport in the matrix, so that for bromide, $\tau_p = 1480$, for HDO, $\tau_p = 1100$ min, and for PFBA, $\tau_p = 4490$. The characteristic time of diffusion for bromide is based on the best fit to the test C data, as discussed in the previous section, and the others are scaled using the diffusivity values given in Table 1.

The predicted separation of breakthrough curves in test C are shown in Figure 6. It is clear that PFBA should break through very differently than HDO and bromide if diffusive transport is responsible for the breakthrough tailing in test C. As can be seen in Figure 3, no such separation is evidence in the data. Similar separations were predicted for the breakthrough tails in all of the tests, but none were observed (see, for example, Figure 4). We must conclude that diffusive transport, either into the rock matrix or in the fracture, was not responsible for the breakthrough tailing observed in these experiments.

5.5. Advective and Hydrodynamic Processes

The observation that breakthrough tailing is independent of the rate of tracer molecular diffusion suggests that a diffusion-like advective process is responsible for the tailing behavior in these tests. Hydrodynamic dispersion is an advective process that resembles diffusion, but a simple one-dimensional advection-dispersion model cannot account for the extended tailing of the tracer breakthrough. We postulate that a more complex dispersive mechanism dominates transport in these tests.

Using hydraulic testing in discrete borehole intervals, *Shapiro and Hsieh* [1998] found that hydraulic conductivity in these rocks vary over 6 orders of magnitude. It is possible that the hydraulic conductivity structure of the bedrock at Mirror Lake is so heterogeneous that noncontinuous transport processes affected the tracers. Transport may occur primarily by rapid advection in higher-conductivity channels and by very slow advection in secondary fractures. These secondary fractures may be on the scale of centimeters to meters and may be associated with stress features of the larger fractures. Mass transfer between these regimes could resemble a diffusive exchange, thus producing a tracer breakthrough curve that falsely implies a significant influence of matrix diffusion.

Tailing may also be due to advective exchange between immobile and mobile fluid fractions in the primary fractures. *Raven et al.* [1988] hypothesized that laminar eddies develop along rough fracture walls and act as a transfer mechanism between mobile and immobile fluid. Indeed, fluid mechanics predict the formation of laminar eddies in channels with widely varying aperture [*Pozrikidis*, 1987]. It should be noted, however, that mass transfer across streamlines in vortices should be some function of the rate of molecular diffusion of the tracer. Consequently, even in the case of advective mass exchange, one might expect tracers of different diffusivity to transport differently.

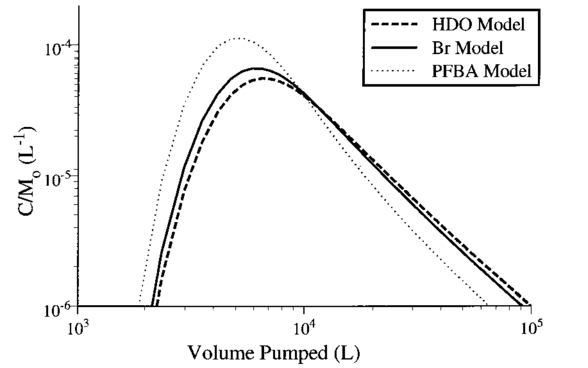

Figure 6. Fit of matrix diffusion model to the bromide data given in Figure 5 compared to the same model adjusted to account for molecular diffusivity of other tracers (τ_p is 1100 and 4490 min for HDO and PFBA, respectively).

It is interesting to note that the late time breakthrough data exhibit a slope of approximately −2 when plotted on a log-log plot (Figures 2–4), whereas the matrix diffusion model (appendix, (6) or (9)) predicts a late time breakthrough slope of −3/2 [*Tsang*, 1995]. The −3/2 slope has been suggested as a "telltale" indicator of matrix diffusion by some researchers [*Tsang*, 1995; *Meigs et al.*, 1996]. Where other slopes have been observed, modified matrix diffusion models have been suggested [*Haggerty and Gorelick*, 1995]. The data presented herein imply that it may not be correct to assume, without corroborating evidence, that experimentally observed breakthrough tailing is caused by diffusion processes alone. In some situations, alternative conceptual models may be needed to explain breakthrough tails.

The breakthrough curves collected at Mirror Lake exhibited the same overall shape regardless of pumping rate, indicating that the rate of apparent diffusion into the matrix (as given by τ_p) changes proportionally with the rate of advective transport in the fracture (as given by τ). This relationship implies that the observed breakthrough tailing is an expression of hydrodynamic transport, and the extending tailing implies that this hydrodynamic transport is non-Fickian in nature. Such a hypothesis seems justifiable, in light of theoretical investigations that predict Fickian transport will occur only after the tracer traveled a sufficient distance to encounter a statistically significant hydraulic conductivity distribution [*Gelhar et al.*, 1979]. This sufficient distance is expected to be large or even infinite in highly heterogeneous media such as fractured rock [*Matheron and de Marsily*, 1980; *Neretnieks*, 1983]. The only way to test this hypothesis, however, is to repeat these tests between wells separated by different distances. These tests have not yet been performed at Mirror Lake.

6. Conclusions

The experimental methods and theoretical interpretation presented herein make it unlikely that injection artifacts, flow field effects, or matrix diffusion caused the breakthrough tailing observed in these tracer experiments. In fact, because tracers of varying diffusivity produced identical late time breakthrough, the data imply that breakthrough tailing was not caused by any purely diffusive transport mechanism. We are left therefore with the conclusion that breakthrough tailing in these tests resulted from a hydrodynamic transport mechanism, such as advection or hydrodynamic dispersion. We hypothesize that this advection-dominated tailing results from the highly heterogeneous spatial and temporal nature of transport in fractured rock.

The tracer tests conducted at Mirror Lake also have implications for the proper execution and interpretation of tracer tests in fractured rock. As noted in section 5.1, the early time tracer breakthrough in these tests was not repeated at different transport velocities, while the late time breakthrough was extremely consistent. This casts suspicion on the practice of fitting models to only the early time breakthrough data [e.g., *Welty and Gelhar*, 1996] or fitting the early time data separately from the late time data [e.g., *Moench*, 1995] in heterogeneous fractured media such as crystalline rock. Our experience indicates that repeating forced gradient tracer experiments using different hydraulic configurations and employing multiple tracers may reveal important information about transport and increase the likelihood of a unique interpretation of the breakthrough data.

Appendix

The model described here assumes that transport occurs by advection and dispersion in the fracture, coupled with molecular diffusion perpendicularly into the bulk rock, in the manner described by *Tang et al*. [1981] and *Maloszewski and Zuber* [1985]. It is assumed that there is no advection in the rock matrix, the matrix is completely homogeneous and isotropic, and it extends infinitely away from the fracture. As applied here, the model also accounts for tracer holdup in the injection system and the reinjection of traced water characteristic of the weak dipole tests [*Becker and Charbeneau*, 2000]. The governing transport equations are

$$\frac{\partial C_f}{\partial t} - v\,\frac{\partial C_f}{\partial x} + D\,\frac{\partial^2 C_f}{\partial x^2} - \frac{n_p D_p}{b}\,\frac{\partial C_p}{\partial y}\bigg|_{y=b} = 0, \qquad (1)$$

$$\frac{\partial C_p}{\partial t} - D_p\,\frac{\partial^2 C_p}{\partial y^2} = 0 \qquad y \ge b, \qquad (2)$$

where x is the spatial coordinate taken to be positive in the direction of flow in the fracture, y is the direction of transport in the matrix perpendicular to the fracture, v is the average linear velocity of fluid flow in the fracture, D is coefficient of hydrodynamic dispersion in the fracture, b is the half-aperture of the fracture, n_p is the porosity of the matrix, and C_f and C_p are the concentrations of tracer in the fracture and matrix, respectively. D_p is the coefficient of effective molecular diffusion in the matrix, where $D_p = FD^*$, D^* is the rate of diffusion in free water, and F is the formation factor [*Skagius and Neretnieks*, 1986].

We apply the following boundary conditions to (1) and (2), respectively,

$$C_f(a, 0) = 0, \qquad C_f(0, t) = \frac{M_0}{Q_f}\,\delta(t), \qquad C_f(\infty, t) = 0, \qquad (3)$$

$$C_p(y, x, 0) = 0, \qquad C_p(b, x, t) = C_f(x, t), \qquad C_p(\infty, x, t) = 0, \qquad (4)$$

where M_0 is the tracer mass injected into the fracture, Q_f is the flow rate through the fracture, and a is the transport length of interest in the direction of flow in the fracture. Solving (1) and (2) subject to (3) and (4) via the Laplace transform with respect to s produces the following:

$$\frac{Q_f\bar{C}(s)}{M_0} = \exp\left\{\frac{av}{2D}\left[1 - \sqrt{1 + \frac{4Ds}{v^2}\left(1 + \frac{n_p}{b}\sqrt{\frac{D_p}{s}}\right)}\right]\right\}. \qquad (5)$$

The overbar represents variables that have been transformed to Laplace space.

For purposes of fitting data it is convenient to reduce the number of parameters in the equation. We rewrite (5) as

$$\frac{\bar{C}(\sigma)}{C_o} = \exp\left\{\frac{Pe}{2}\left[1 - \sqrt{1 + \frac{4\sigma}{Pe}\left(1 + \sqrt{\frac{\tau}{\tau_p\sigma}}\right)}\right]\right\}, \qquad (6)$$

where

- Pe Peclet number, equal to $(va)/D$;
- τ characteristic time of advective transport in the fracture, equal to a/v;
- τ_p characteristic time of diffusive transport into the matrix, equal to $b^2/(n_p^2 D_p)$;
- C_0 initial concentration of tracer mass in the fracture, equal to $\tau Q_f/M_0$
- σ dimensionless Laplace transform variable, equal to $s\tau$.

Becker and Charbeneau [2000] showed that the boundary conditions given in (3) correspond to that of the first passage time solution of the advection-dispersion equation. This allows us to treat (6) as a transfer function $\bar{F}_T$, given in Laplace space by

$$\bar{F}_T = \bar{C}(\sigma)/C_0. \qquad (7)$$

Furthermore, because the injection system appears to be fully mixed (see section 3), it may also be treated as a transfer function decreasing exponentially over time $\bar{F}_S$, given in Laplace space by

$$\bar{F}_S = \gamma/(\gamma + \sigma), \qquad (8)$$

where γ is the ratio of mean travel times in the formation and injection system (or τ/τ_s, where τ_s is the mean residence time of tracer in the injection system).

For weak dipole tracer tests it is also necessary to account for the injection of traced fluid extracted by the pumping well back into the injection system. In Laplace space this may be accomplished using the algebraic function,

$$\bar{F}^* = \left[\frac{\bar{F}_S\bar{F}_T}{1 + \varepsilon(1 - \bar{F}_S\bar{F}_T)}\right], \qquad (9)$$

where $\bar{F}^*$ is the transfer function that accounts for transport in the formation, as well as mixing in the well bore and reinjection. The coefficient ε represents the fraction of pumped fluid that is reinjected. In the specific case of the Mirror Lake weak dipole tracer tests, $\varepsilon = 0.05$.

Model calculations used in this article were accomplished by substituting (6), (7), and (8) into (9) and taking the inverse Laplace transform. Laplace transform inversion was accomplished numerically using a MathCad spreadsheet that utilizes a fast Fourier transform algorithm. This method was found to compare favorably by the algorithm proposed by *de Hoog et al*.

[1982] and discussed by *Moench* [1991]. Fitting of data was accomplished by manually altering the Peclet number and the characteristic times of transport in the fracture and matrix, τ and τ_p, respectively. Goodness of fit was determined by visual inspection.

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M. W. Becker, Department of Geology, State University of New York at Buffalo, 876 Natural Science Complex, Buffalo, NY 14260. (mwbecker@geology.buffalo.edu)
A. M. Shapiro, U.S. Geological Survey, 12201 Sunrise Valley Drive, Reston, VA 20192.

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