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Nonclassical Transport Processes in Geologic Media: Review of Field and Laboratory Observations and Basic Physical Concepts

Leonid Bolshov, Peter Kondratenko,* Karsten Pruess,* and Vladimir Semenov

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We present an overview of the problem of solute transport in unsaturated heterogeneous media. We first review field and laboratory observations that demonstrate nonclassical flow and transport behavior. The main physical principles causing anomalous transport regimes in fractured rock media are identified. The basic factors and physical concepts needed to describe anomalous transport in saturated and unsaturated fractured rock are discussed in detail.

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NUMEROUS STUDIES over the years have focused on the problems of fluid flow and solute transport in geologic media (National Research Council, 1996). These processes are of special importance when investigating future geologic repositories for radioactive wastes. A large body of field and laboratory observations now exists that indicates that standard hydrologic models based on Darcy's and Fick's laws in many cases give inaccurate predictions of the spatial and temporal characteristics of transport phenomena in heterogeneous geologic media. The complex nature of transport in such media requires the development of new theoretical approaches, experimental methods, and numerical techniques.

This review was the first step in developing mathematical modeling approaches for flow and transport processes in variably saturated heterogeneous and fractured media (Dykhne et al.,

2008; Bolshov et al., 2008; Goloviznin et al., 2008). Our aim was to review field and laboratory observations that illustrate the fundamental mechanisms of flow and transport, and to provide an introduction to our development of the main physical and mathematical concepts that, in our view, provide a basis for describing transport processes in geologic media. Our review is rather cursory and not intended to provide a comprehensive discussion of experimental evidence for nonclassical transport in geologic media. The literature on the subject is extensive. Only a limited number of references are given of cases where anomalous transport properties have been observed. The references cited reflect our interest and experience. Our goal was to provide an experimental background for the physical and mathematical approaches developed here and in Dykhne et al. (2008), Bolshov et al. (2008), and Goloviznin et al. (2008). For a more detailed discussion of recent approaches to modeling transport in highly heterogeneous media, we refer to Sahimi (1995), National Research Council (1996, 2001), and Faybishenko et al. (2000b).

Laboratory and Field Observations of Nonclassical Transport in Geologic Media

Anomalous flow and solute transport properties of heterogeneous media are encountered in both laboratory experiments with small-sized samples and field-scale investigations of the vadose zone and groundwater aquifers. Natural fracture networks often provide the main pathways for fluid flow and solute transport. Direct investigations of their geometric characteristics can yield important information about the underlying flow and transport

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processes. Most of the field experiments surveyed here were conducted in saturated, fractured aquifers. Although fluid flow in unsaturated rocks has its own unique features, the main processes determined by the heterogeneity and disorder of the media also reveal themselves under saturated conditions.

Laboratory Experiments

It is well known that the process of moisture penetration in unsaturated, homogeneous, porous materials owing to capillary forces may be described by a nonlinear diffusion equation exhibiting $t^{1/2}$ time dependence of the absorbed mass (Bazant and Najjar, 1972; Hall and Yau, 1987; Daian, 1988; Hall, 1989; Hall and Hoff, 2002; Gummerson et al., 1979; Carpenter et al., 1993; Pel, 1995). Several experimental studies have shown, however, that absorption of water in such natural materials as limestone, brick (Küntz and Lavallée, 2001), and cement-based materials (Hall et al., 1995; Taylor et al., 1999) can deviate from the classical $t^{1/2}$ law. The total amount of water absorbed by a sample in an experiment by Küntz and Lavallée (2001) was found to be proportional to t^γ , with $\gamma = 0.6$ (i.e., $\neq 0.5$).

The nature of the observed anomalous flow behavior is not clear. Theoretical studies based on the assumption of explicit time dependence of the diffusivity (e.g., Lockington and Parlange, 2003), as well as numerical models (e.g., Küntz and Lavallée, 2003), have shown good agreement with the data but were mostly phenomenological and did not provide any physical explanation. It is not clear from the experiments and models whether the observed transport regimes were mostly transient or asymptotic (i.e., corresponding to large times t). But even if they were transient, the existence of nonclassical behavior is of principal importance for understanding fluid flow and solute transport in real permeable media. Nonclassical behavior of solute transport has been observed in many experiments with artificial models of soil consisting of small porous glass beads (Scheven and Sen, 2002; Sternberg, 2004), which showed that solute concentration profiles have a non-Gaussian form.

Numerous experimental studies of solute transport at scales from one to several meters have been performed in recent decades on columns of natural soil (Porro et al., 1993; Zhang et al., 1994; Khan and Jury, 1990) as well as in field plots (Ellsworth et al., 1996; Yasuda et al., 1994; Snow et al., 1994; Jury, 1988). The results of solute concentration measurements at different depths in these experiments have been generalized by Pachepsky et al. (2000). They found that solute behavior generally does not obey the classical advection–diffusion equation. The dispersivity (defined as the dispersion coefficient divided by the mean fluid velocity) inferred from matching the advection–dispersion equation with the data was found not to be constant but to increase with the distance traveled by the solute tracer. Experiments showing the solute dispersivity increasing with depth have been reported also by Jaynes et al. (1988), Butters and Jury (1989), Hamlen and Kachanoski (1992), and Jaynes and Rice (1993).

The scale dependence of infiltration and transport phenomena can manifest itself in many ways (Neuman and Di Federico, 2003; Zlotnik et al., 2000). Data presented in a review by Neuman and Di Federico (2003) show evidence that such hydraulic variables as permeability and dispersivity depend on the scales of measurement, observation, the sampling window (domain of investigation), and spatial resolution. Measurements of

permeability on a 1-m sandstone block using a specially designed permeameter attached to the rock surface with a rubber tip seal (Tidwell and Wilson, 1997, 1999) showed that the sample mean permeability increased systematically with contact size (inner radius of tip seal). Other manifestations of hydrogeologic scaling of field observations are discussed below.

Cortis and Berkowitz (2004) analyzed several classical experiments on dispersion of a passive tracer in porous columns (Jardine et al., 1993; Nielsen and Biggar, 1962). They found that the breakthrough curves (BTCs) exhibited anomalous (non-Fickian) behavior at early times, and late-time tailing. A typical BTC obtained by Nielsen and Biggar (1962), together with best fits with the classical advection–diffusion model and the continuous-time random walk model, is shown in Fig. 1.

The problem of relating transport properties with pore space geometry has been addressed in several studies (e.g., Perfect and Sukop, 2001; Hunt, 2004a; Hunt and Gee, 2002). In many cases, the particle- and pore-size distributions measured for samples of real soil (Hunt and Gee, 2002) obey a power law in some size range. The porous volume presents then a random fractal. While the pore volume may be well connected by itself, even under saturated conditions, only a fraction of the channels will carry significant flow because of high hydraulic resistances of channels with small radii. As shown by Hunt and Gee (2002), the mean permeability can be estimated using critical path analysis. At low saturation when the moisture content is reduced to a minimal value (below which fluid breaks up into unconnected parts), capillary flow paths form a percolation cluster with a fractal structure (Hunt, 2004b). We note that the fractal dimension of the percolation cluster need not be the same as that of the pore space.

FIG. 1. Measured breakthrough curve (BTC) for unsaturated Oakley sand column (circles; Nielsen and Biggar, 1962): flux-averaged concentration j vs. pore volumes. The upper figure presents the complete BTC, while the lower figure shows early-time behavior. Velocity $V = 1.03 \text{ cm h}^{-1}$, column length = 30 cm. Dashed lines show the best fit with the classical advection–diffusion equation (ADE) model; solid lines show the best fit with the continuous-time random walk (CTRW) model (taken from Cortis and Berkowitz, 2004).

A large number of laboratory experiments have been conducted for the purpose of investigating infiltration into separate natural cracks under saturated (Raven and Gale, 1985; Pyrak-Nolte et al., 1987; Durham and Bonner, 1994; Keller et al., 1995; Vandergraaf, 1995; Nolte et al., 1989) and unsaturated conditions (Nicholl et al., 1993; Rasmussen, 1991; Rasmuson and Neretnieks, 1986; Persoff and Pruess, 1995). Water flow within actual fractures may differ strongly from flow between two smooth parallel plates. Strongly irregular fracture wall surfaces can lead to flow anisotropy and also to a violation of the well-known cubic law that holds for smooth surfaces (Vandergraaf, 1995). The irregular roughness of fracture walls may result in flow exhibiting stochastic properties, even at small scales (5–40 cm); preferential pathways and flow channeling may then become apparent (Tsang and Tsang, 1987; Tsang and Neretnieks, 1998), with up to 90% of the flow passing through only 5 to 20% of the exit section (Rasmuson and Neretnieks, 1986; Su et al., 1999). Under such conditions, anomalous dispersion of transported solutes is to be expected (Roux et al., 1998).

Field Experiments: Investigation of the Fracture System

Field experiments are conducted in connection with problems of irrigation in agriculture, assessment of soil and groundwater quality and contamination, water supply, oil and gas reservoir exploration and exploitation, and characterization of radioactive waste repository sites (Karasaki et al., 2000). Studies of the geometric characteristics of fracture systems can be conducted under laboratory conditions as well as in field settings, including outcrops and mine drifts where fracture traces are mapped on exposed rock surfaces or borehole walls (Odling, 1997; Bonnet et al., 2001).

Fracture systems have been studied extensively for at least 30 yr. Information on fracture statistics (e.g., distributions of length, aperture, and orientation) has been derived mainly from two-dimensional maps of fracture traces in planes intersecting a three-dimensional fracture network. Such maps may have been created from field data, aerial photographs, and satellite image analyses, and have covered a wide range of sample sizes (from centimeters to kilometers). Data collected in a review by Bonnet et al. (2001) show that in many (but not all!) cases these distributions follow a power law without any characteristic spatial scale.

Two-dimensional fracture networks (i.e., traces of three-dimensional networks) often exhibit fractal properties. A large number of experimental data on estimated fractal dimensions of fracture networks were analyzed and generalized by Bonnet et al. (2001). They found a wide spectrum of fractal dimensions covering the theoretically possible range (between 1 and 2), with two maxima at values of 1.5 and 2. Fracture patterns with a dimension of 2 are not fractal, while the value of 1.5 may correspond to three-dimensional fracture networks with a fractal dimension of 2.5 (Bonnet et al., 2001). Note that 2.5 is close to the fractal dimension of a network percolation cluster (Sahimi, 1993).

When considering fluid flow in rocks, the most important properties of the fracture network are their interconnections. For random fracture emplacement, connectivity may be treated as a percolation problem (Madden, 1983). Percolation theory (Isichenko, 1992; Stauffer and Aharony, 1992; Berkowitz, 1995) indeed may be a very suitable tool for analyzing flow and transport in fracture networks. Continuum percolation, as discussed

by Berkowitz and Ewing (1998), is the most appropriate model in this case, as it better represents a network structure than standard lattices (Perfect and Sukop, 2001). Percolation networks require a parameter that determines how close the fracture system is to the percolation threshold. Theoretical approaches developed by Madden (1983) imply that the relevant parameter is the normalized fracture density. Experimental data on crack statistics and connectivity with natural fractured granite samples (Hadley, 1975; Simmons et al., 1975; Wong, 1980) have proved theoretical results on the onset of permeability through the sample and the onset of mechanical failure. Sample failure implies conductivity existence but not vice versa.

The percolation threshold is crucial for describing transport processes in fracture systems. Much attention has been devoted to calculating critical parameters for mathematical models of fracture networks (Mourzenko et al., 2005; Adler and Thovert, 1999). Mourzenko et al. (2005) numerically studied a three-dimensional network model with cracks of regular polygonal form having a power-law size distribution. The relevant percolation parameter in such a system is the dimensionless fracture density normalized by the third moment of the fracture size distribution. For networks of regular polygons, the dimensionless critical fracture density depends only slightly on the fracture size distribution and on the shape of the fractures.

Conditions and processes near the percolation threshold are of particular interest. In many applications, the medium may be considered close to the threshold. This is indirectly justified by mechanical considerations that suggest that stress relief takes place when the fracture network reaches the percolation threshold (Gueguen et al., 1999). Local fracture permeabilities may span a large range, typically four orders of magnitude or more (Karasaki et al., 2000; Ando et al., 2003). Therefore, a small part of the fractures may often carry the major part of the flow, and even seemingly well-connected networks may turn out to be actually near the percolation threshold (Berkowitz, 2002).

Significant progress has been made recently in investigating the properties of surfaces confining natural cracks. Profilometer measurements have shown that their relief is characterized by extreme nonregularity and self-affine fractal properties (Brown and Scholz, 1985; Poon et al., 1992; Schmittbuhl et al., 1995). These properties, which are observed regardless of rock type and crack origin (Berkowitz, 2002), in themselves can lead to anomalous effects during transport in individual fractures (Roux et al., 1998). All this suggests that theories of flow and transport through fracture networks should include a description of the network on the basis of known properties of percolation systems.

Borehole Hydraulic Tests

One common field method is hydraulic testing (pumping or transient pressure tests) in which hydraulic head variations with time at different locations are observed in response to the withdrawal of water from (or injection into) a borehole. Proper interpretation of the test results requires knowledge of the geometric characteristics of the medium, in particular the dependence of the cross-sectional area A of flow on the distance r from the source. For three-dimensional homogeneous geometries (unconfined porous media), we have $A \propto r^2$, for two-dimensional geometries (confined flat layer or parallel regular fracture systems) $A \propto r^1$, and for one-dimensional geometries (systems of constant

aperture channels) $A \propto r^0$. Experiments in fractured rocks often give results that cannot be interpreted on the basis of these relationships for any dimension. This is a fundamental difference between fractured media and porous media with predominant intergranular permeability (Novakowski and Bikerton, 1997; Chang and Yortsos, 1988, 1990; Riemann and van Tonder, 2002a,b,c).

Many studies of transient regimes in hydraulic tests (Chang and Yortsos, 1988, 1990; Riemann and van Tonder, 2002a,b; Acuna and Yortsos, 1995) have suggested that the pore space in subsurface reservoirs and aquifers may have a fractal structure. The cross-sectional area A for flow in such media would depend on the distance from the source r as $A \propto r^{n-1}$, where n is in the range $1 < n < 3$ and, in general, not an integer. This is in contrast with homogeneous media, where n is always an integer. The parameter n is termed the *flow dimension* (Riemann and van Tonder, 2002a; Barker, 1988).

Riemann and van Tonder (2002b,c) used these ideas to interpret hydraulic test results for a fractured aquifer of relatively large size, about 200 by 200 m² (i.e., the Campus Test Site located at the University of the Free State, Bloemfontein, South Africa). They showed that simulation of the constant-rate transient withdrawal tests using a generalized model assuming fractional values of n results in good agreement with the observed data. Best-fitted values of n for two boreholes in different parts of the site were found to be 1.75 and 1.85 (i.e., they were nonintegral). Similar findings have been reported by others (e.g., Filho, 2003; Beauheim et al., 2002; Walker and Roberts, 2002; Jourde et al., 2002; Doe, 1991; Becker and Charbeneau, 2000), thus indicating that the geometric properties of permeable geologic media cannot be described with the classical integral values of n . This provides further field evidence of the fractal structure of the conductive fracture and channel network.

Fluid flow in fractured media generally shows a complicated structure that sometimes cannot be characterized by a unique value of the index n . Examples of such media are given by Beauheim et al. (2002). This finding may be related to a possible lack of self-similarity of fracture systems at all scales (Jourde et al., 2002), nonstationary effects (Walker and Roberts, 2002), or the difference in volumes investigated by tests of different types (Walker and Roberts, 2002). Thus, the results of hydraulic tests in fractured rocks of low intrinsic permeability in many cases lead to the conclusion that the fracture network in the test region has a fractal structure and that flow cannot be described on the basis of approximations applicable to uniform media having averaged properties.

Tracer Tests

Tracer experiments are widely used for characterizing field sites. Different designs may be used (Becker and Charbeneau, 2000; Becker and Shapiro, 2000; Widestrand et al., 2001; Dillon et al., 2003), such as tracer injection into one well and concentration monitoring at offset wells, convergent flow involving pumping of water from one of the wells, or using a dipole configuration with pumping from one well and injection into another. The main information about the dispersion and sorption properties of the medium is contained in tracer breakthrough curves [the time-dependent tracer concentration in a well being monitored, $c(t)$]. A typical feature of fractured rocks (compared with media with predominant intergranular porosity and permeability)

is early breakthrough followed by extensive late-time tailing. This tailing usually is caused by tracer diffusion into conductive channel walls and the processes of adsorption–desorption onto the walls (Shan and Pruess, 2005).

Still, a number of experiments exist where tailing may be unrelated to diffusion into matrix walls (e.g., Becker and Shapiro, 2000). For different tracers with large differences in sorption behavior and diffusivity, late-time tailing was found to be similar and of a power-law form, $c(t) \propto t^{-\delta}$, with $\delta \sim 1.7$ to 1.8 as evaluated from data given by Becker and Shapiro (2000). Such values for δ conform to neither a classical diffusion mechanism for tail formation nor classical dispersion in a quasi-uniform medium. Early-time tailing in the study by Becker and Shapiro (2000) was found to be exponential:

$$c(t) \propto \exp \left[- \left(|\mathbf{r} - \mathbf{u}t| / dt^\gamma \right)^{1/(1-\gamma)} \right] \quad [1]$$

where $\mathbf{r}$ is the distance between the initial plume center and the sampling location, $\mathbf{u}$ is the drift velocity, and d is the effective “diffusivity.” Application of Eq. [1] to the data of Becker and Shapiro (2000) leads to $\gamma \sim 0.6$, which is different from classical dispersion where $\gamma = 0.5$. This result provides evidence for anomalous dispersion related to stochastic advection in a fractal fracture system.

Different results were obtained by Widestrand et al. (2001) in an experiment with tracers having different sorptivities and diffusivities. Interaction with the matrix played only a minor role for some of the tracers. Late-time concentration tails of these tracers closely coincided with each other and followed a power law with $\delta \sim 3.1$. Thus, the data reported by Widestrand et al. (2001) may also be interpreted as demonstrating anomalous dispersion in fractured rocks.

An experiment involving the injection of an inert tracer (not interacting with the matrix) was conducted by Dillon et al. (2003) in a groundwater system surrounding a high-volume wastewater disposal well in the Florida Keys. The aquifer was in limestone with cracks, channels, and pores of all scales. From the data in Dillon et al. (2003), the dependence on travel distance of arrival time and the maximum tracer concentration at a remote well could be evaluated. While results showed considerable scatter in the data, they did provide strong evidence that dependence on distance was very different from classical expectations for a uniform permeable medium. These findings again provide evidence of anomalous dispersion due to stochastic advection in fractured rocks.

Nonclassical (non-Fickian) behavior at early and late times (tailing of solute breakthrough curves) and scale-varying hydraulic and transport characteristics is generally the rule rather than the exception for tests in fractured media (Silde et al., 1998; McKay et al., 2000; Kosakowski et al., 2001). To better describe the results of such tests, Gelhar et al. (1992) and Rajaram and Gelhar (1995) proposed the concept of scale-dependent dispersion. By analogy with turbulent diffusion in the atmosphere, dispersion is then assumed to depend on the dimensions of the solute plume since it is determined by flow velocity variations on a scale comparable to, or less than, the plume dimensions. It should be noted that interpretations of tracer tests in fractured media often are possible only at a qualitative level due to the complexity of the flow geometry of natural fracture networks.

In experiments of this type, the transport of an injected tracer pulse is investigated without being affected by artificial perturbations from pumping or injection wells. Detailed descriptions have been published for natural-gradient tracer tests at a site on Cape Cod, Massachusetts (LeBlanc et al., 1999) and the macrodispersion experiment (MADE) at the Columbus Air Force Base in Mississippi (Adams and Gelhar, 1992; Boggs et al., 1993). Both tests were conducted with rather fine spatial and temporal resolution of the monitoring borehole network, thus allowing the plume profile and evolution to be traced in great detail.

In both cases, the aquifer was a sand–gravel mixture containing also silts, clays, and rock fragments (boulders), giving rise to extreme heterogeneity with a wide range in local permeability values. In both tests, the volume increase of the tracer plume with time was found to be anisotropic: vertical dispersion was very small, with dispersion taking place primarily in the horizontal direction. Plume growth in the longitudinal direction was considerably faster than expected from the classical Fickian law:

$$R(t) \propto t^\gamma \quad [2]$$

where $R(t)$ is the longitudinal plume size as a function of time t . Results showed $\gamma \sim 0.87$ for MADE (Adams and Gelhar, 1992; Boggs et al., 1993) and $\gamma \sim 0.6$ for Cape Cod (LeBlanc et al., 1999). Data about the temporal evolution of the maximum and averaged concentrations in the plume were in good agreement with the spatial analysis. The MADE-2 experiment (Boggs et al., 1993) revealed that the concentration profile was asymmetric in the direction of average flow: the trailing tail was strongly elongated and had a power-law form rather than being exponential. These results show that tracer dispersion in highly heterogeneous aquifers is anomalous and cannot be described on the basis of the classical diffusion approach. More detailed analyses of the experimental data are given by Meerschaert et al. (2001) and Benson et al. (2001).

Another example of tracer plume behavior was discussed in a review by Neuman and Di Federico (2003). Their analysis involved an experiment conducted under natural hydraulic gradient conditions in a shallow, anisotropic sand aquifer at the Canadian Forces Base, Borden, ON, Canada (Sudicky et al., 1983; Mackay et al., 1986; Roberts and Mackay, 1986; Roberts et al., 1986). The measurements unambiguously showed that plume behavior could not be predicted with Fick's law at comparably early times: both longitudinal and transverse dispersivities increased with travel time (or with travel distance). At later times (large distances), a quasi-Fickian regime was established in which the dispersivity became constant. This behavior arises from heterogeneities with finite correlation length ξ (Neuman and Di Federico, 2003). There are spatial fluctuations in soil properties (permeability and porosity) that are correlated at distances $l < \xi$. At large distances, these fluctuations are not correlated and the medium becomes statistically homogeneous. The non-Fickian regime may be explained by the fact that, as the plume grows, it gradually encounters heterogeneities on larger and larger scales. The Fickian regime is eventually reached when the plume size becomes greater than ξ , at which time the medium becomes statistically homogeneous (Neuman and Di Federico, 2003).

A major question concerning the conductive properties of unsaturated fractured rocks is the basic mechanism governing fluid flow in such media. According to classical capillary theories (Wang and Narasimhan, 1985; Peters and Klavetter, 1988), water, owing to capillary effects, is absorbed by the rock matrix and spreads due to flow through it. In this case, fractures are obstacles for water flow across large distances. For fractured tuffs with low matrix permeability, such as those at the potential waste repository at Yucca Mountain, alternative concepts for water flow may be needed. One possible concept views cracks as the main pathways for water flow, while capillary absorption is a relatively minor effect (Pruess et al., 1999; Pruess, 1999; Liu et al., 1998). Under such conditions, water flow is extremely nonuniform and nonstationary, and subject to preferential flow along localized pathways (Foster and Carington, 1980; Faybishenko et al., 2000a).

Water flow and solute transport are determined not only by the statistical properties of the fracture network but also by the degree of fluid saturation and fracture–matrix interactions. As mentioned above, at low saturation even a well-connected network cannot conduct since the fluid volume is disconnected. Flow is possible only when saturation exceeds the percolation threshold. Unfortunately, up to now only a few experimental investigations of water flow and solute transport have been conducted in unsaturated, fractured rocks. Studies by Dahan et al. (1998, 1999, 2000) described field experiments in unsaturated fractured chalk that showed spatial and temporal flow instabilities and channeling, with most of the flow (70–100%) passing through only a small part of the accessible fractures (15–20%). In this case, the active water flow paths fluctuated in dependence on wetting–drainage cycles, while chemical interactions occurred between the flowing water and the fracture walls involving the dissolution of minerals. These effects significantly complicated the seepage patterns in the unsaturated zone compared with saturated flow.

A study by Huang et al. (1999) described the results of pneumatic tests conducted in a tunnel at Yucca Mountain using an array of boreholes of 5- to 10-m length, drilled in various directions. Air was injected into one isolated borehole interval while the pressure was monitored in other intervals along the same and surrounding boreholes. The test data made it possible to estimate permeability near each borehole (single-hole test) as well as in a larger region between boreholes covered by air flow (cross-hole tests). From these data, a three-dimensional permeability map of the domain was inferred by calibrating numerical models with the TOUGH2 computer code (Pruess, 2004). Although the data could not provide a complete characterization of the fracture network structure in the area under investigation, they did provide information about local permeability variations. These variations were found to be very large, spanning approximately five orders of magnitude. Observations of rapid pressure responses indicated that all of the wells were well connected by a fracture network, at least pneumatically.

Neuman and Di Federico (2003) later noted that single-borehole tests (which tend to sample smaller rock volumes than cross-hole tests) generally yield lower permeability values. This is one more manifestation of hydrologic scaling. Analogous results were obtained by Chen et al. (2000) in pneumatic experiments conducted in a borehole array penetrating unsaturated fractured

tuff at the Apache Leap Research Site near Superior, AZ. They found that local values of the permeability inferred from pneumatic tests varied across a wide range (three to four orders of magnitude). Measured permeability values at different points obtained from single-hole tests proved to be spatially correlated. Geostatistical analyses showed that the data could be described by a power-law variogram (Chen et al., 2000). This implies that the data represented a sample of random fractal permeability with no correlation scale. Water flow in such a medium should deviate from classical behavior.

Factors Determining Anomalous Transport in Fractured Media

One of the key factors determining fluid flow and tracer transport in geologic media is the geometry of the fracture system. As indicated above, fracture systems as a rule can be classified as percolation media. The flow and transport characteristics of such media are determined by the connectivity property of their structural elements (in the case of geologic media, these are fractures completely or partially filled with water). Such elements combine into clusters inside of which fluid flow and solute transport are effective, while these processes between separate clusters are weak.

Two characteristics of percolation media are most important. One is the existence of a percolation threshold. Below the percolation threshold, there are only finite clusters and stationary processes of moisture infiltration in the infinite medium are ineffective. Above the percolation threshold, the medium contains an infinite cluster and transport is not limited with respect to spatial range.

A second characteristic of percolation media is the correlation length ξ . Below the percolation threshold, cluster sizes l are in the range $l < \xi$ (the number of clusters with length scale $l > \xi$ is exponentially small). In this case, each individual cluster in the scale interval from a certain value a , which we call the *lower truncation size*, to the dimension of the cluster itself, has fractal properties (see Mandelbrot, 1982). This means that the cluster, as a geometric object, has not an integral but a fractal space dimension. On approaching the percolation threshold, the correlation length tends to infinity, $\xi \rightarrow \infty$, and an infinite cluster arises in the medium. Above the percolation threshold, the parameter ξ becomes finite again. The percolation medium is fractal at scales $a < l < \xi$ and is statistically homogeneous at scales $l > \xi$.

There is no specific spatial scale to characterize the behavior of the fracture system in the length interval $a \ll r \ll \xi$. This makes it possible to take advantage of the concepts of the theory of critical phenomena (Patashinskii and Pokrovskii, 1979; Ma, 1976) and to consider water flow and tracer transport processes across length scales r with $a \ll r \ll \xi$ to be scale invariant. In other words, one can consider the macroscopic transport equation to be invariant with respect to the transformation

$$\mathbf{r} \rightarrow s\mathbf{r} \quad [3]$$

with all relevant quantities (such as flow velocity, solute flux density, and solute concentration) transforming as

$$B \rightarrow s^{-\Delta_B} B \quad [4]$$

where the exponent Δ_B is termed the *scaling dimension* of the quantity B . While some relationships between the scaling dimensions may be found from conservation laws and the governing macroscopic equations, accurate estimates of the scaling indices requires a more sophisticated analysis.

Knowledge of the scaling dimensions provides considerable insight into the prevailing flow and transport processes. Functional relationships for a single variable become power-like and relationships for two or more variables reduce to the product of a power function and a function depending on self-similar dimensionless variables. An example of the first kind of regularity is the dependence of solute plume size on time expressed by Eq. [2].

A basic mechanism of tracer transport in fracture systems is through advection by flowing water. Percolation systems of fractures tend to be highly disordered, making solute advection a random process. Because of the fractal nature of percolation clusters, correlations of the advection velocity are long ranged (decaying according to a power law). Due to this and because advection is a relatively fast transport mechanism, a superdiffusive transport regime may result when $\gamma > 1/2$ in Eq. [2]. We emphasize that an important aspect of solute transport in geologic media is random advection with long-range velocity correlations. This feature alone can make the transport regime correspond to superdiffusion.

Another important aspect of transport in geologic media arises from sharply contrasting properties caused by the presence of a low-permeability matrix. For solute transport through fractures containing moisture, the matrix plays the role of traps (or sinks and sources), which ultimately cause the infiltration and solute transport process to slow down. Along with this, a percolation cluster has a complicated topological structure, consisting of a backbone and a set of dead ends. The backbone connects remote parts of the cluster, whereas dead ends are connected with the backbone at only one point but remain isolated from each other and from other domains of the backbone. Therefore, with respect to infiltration and transport, dead ends also play the role of traps. It is important to note that the set of dead ends has a fractal dimension that is greater than that of the backbone. The dead ends together with the matrix may be considered as a low-permeability subsystem of the fractured geologic medium, in contrast to the connected fractures, which form a high-permeability subsystem.

With regard to the existence of two contrasting subsystems, all tracer particles may be subdivided into two parts: active particles in the high-permeability subsystem and passive particles residing in the low-permeability subsystem. Of primary interest are the active particles because of their high effective mobility. The presence of a low-permeability subsystem has two important consequences. One is that the number of active particles will decrease with time as some of them become trapped. The second consequence of a low-permeability subsystem is to slow down solute transport by promoting a subdiffusive transport mode with $\gamma < 1/2$ in Eq. [2].

Another important factor is the possibly strong fluctuations in the flow velocity. Such fluctuations arise because of the random structure of geologic media. The evolution of solute concentrations in space and time depends on the specific location of the

initial solute concentration distribution (source region). Therefore, spatial fluctuations in medium characteristics may effectively renormalize the solute source power.

Along with gravity and viscosity, capillary forces play a significant role in unsaturated flow processes. At low saturation, moisture accumulates in the narrowest sections of cracks and is retained there in droplets held by capillary forces. Additional moisture supply causes the droplets to grow and to become unstable after reaching some critical size, thus initiating flow. Fluid flow hence goes through a cascade of transitions between metastable states caused by the action of capillary forces, which makes the process inherently nonstationary. This means that not only spatial but also temporal (dynamic) fluctuations are important for the velocity distribution during unsaturated flow. In addition, dynamic effects may be caused by variable inflow of moisture through the upper boundary of the geologic medium, thereby reflecting seasonal and climatic variations in the precipitation rate.

We now give a qualitative derivation of Eq. [2] for random advection as the basic transport mechanism in a high-permeability subsystem, and taking into account the action of traps caused by a low-permeability subsystem. Suppose that a random advection velocity obeys a stationary distribution with zero average value. We identify the solute plume size $R(t)$ as a root mean square displacement of a solute particle during time t . This occurs as a result of $M_b(t)$ random steps of length b with advection velocity $V(b)$ as follows:

$$R_b(t) \sim b \sqrt{M_b(t)} \quad [5]$$

in which $b \leq R_b(t)$. The actual value of $R(t)$ should be the maximum of $R_b(t)$ with respect to the step length b :

$$R(t) \sim \max_b [R_b(t)] \quad [6]$$

The number of steps $M_b(t)$ entering Eq. [5] is expressed through the quantities $V(b)$ and b by the relation

$$M_b(t) \sim \frac{V(b)\varphi(t)t}{b} \quad [7]$$

where $\varphi(t)$ is the probability for the particle to reside in a high-permeability (active) subsystem. Due to the scaling invariance property expressed by Eq. [3] and [4], $V(b)$ and $\varphi(t)$ should be power functions of the form

$$V(b) \sim V(a/b)^b, \quad a < b < \xi \quad [8]$$

$$h > 0$$

$$V(b) \sim V, \quad b < a$$

$$\varphi(t) \sim \left(\frac{t_*}{t}\right)^{1-\alpha}, \quad t > t_*, \quad 0 < \alpha < 1 \quad [9]$$

The exponent h in Eq. [8] is determined by the rate of decay of the advection velocity correlations. The parameter t_* in Eq. [9] is some lower bound of time related to the lower bound of the fractality interval a . The limits of the exponent α in Eq. [9] result from the obvious requirement that $\varphi(t)$ and $t\varphi(t)$ should be decreasing and increasing functions, respectively.

According to the definition $\varphi(t)$, this function also determines the total number of active solute particles $N(t)$ in the problem with a fixed total number of all solute particles N_0 :

$$N(t) \sim N_0 \varphi(t) \sim N_0 \left(\frac{t_*}{t}\right)^{1-\alpha} \quad [10]$$

Substituting Eq. [8] and [9] into Eq. [7] and then into Eq. [5], we obtain the relation

$$R_b(t) \sim \sqrt{V \left(\frac{b}{a}\right)^{1-b} a \left(\frac{t_*}{t}\right)^{1-\alpha} t} \quad [11]$$

This shows that the maximum of $R_b(t)$ occurs at $b = R_b(t)$ for $h < 1$ and at $b \sim a$ for $h > 1$. Therefore, based on Eq. [6] we obtain

$$R(t) \sim \left(V a^h t_*^{1-\alpha} t^\alpha\right)^{1/(1+h)}, \quad h < 1 \quad [12]$$

$$R(t) \sim \left(V a t_*^{1-\alpha} t^\alpha\right)^{1/2}, \quad h > 1$$

Thus, we have the following expressions for the exponent γ in Eq. [2]:

$$\gamma = \alpha/(1+h), \quad h < 1 \quad [13]$$

$$\gamma = \alpha/2, \quad h > 1$$

These relationships are valid for $R(t) < \xi$. Depending on the values of the exponents h and α , the transport regime may correspond to superdiffusion ($\gamma > 1/2$), classical diffusion ($\gamma = 1/2$), or subdiffusion ($\gamma < 1/2$). Classical diffusion with $\gamma = 1/2$ also takes place in the statistically homogeneous case when $R(t) > \xi$.

It follows from the above analysis that the space and time dependence of the active solute concentration in the main body of the plume has the structure

$$c(\mathbf{r}, t) = \frac{N(t)}{R^3(t)} \Phi(\zeta), \quad \zeta = \frac{r}{R(t)} \quad [14]$$

where $N(t)$ is the total number of active solute particles determined by Eq. [10]. The function $\Phi(\zeta)$ of dimensionless variable ζ has the properties

$$\Phi(0) \sim 1, \quad \Phi(\zeta)|_{\zeta \rightarrow \infty} \rightarrow 0 \quad [15]$$

and provides the proper normalization:

$$\int d^3r c(\mathbf{r}, t) = N(t) \quad [16]$$

The forms of the functions $N(t)$ and $R(t)$ depend on the transport regime. The regime may vary with time due to switching on or off of individual elements (e.g., specific traps). Therefore, the form of these functions will be specific for characteristic time intervals determined by the action of a corresponding transport regime.

Another important element of solute transport, especially for the problem of radioactive waste disposal in geologic media, concerns the asymptotic concentration behavior (i.e., the concentration tails). It is of great practical importance to know whether a concentration tail is power-like or exponential, since at large distances and long times the differences in concentrations between these two functional forms can grow to many orders of magnitude.

Conclusions

This review and analysis shows that a large body of laboratory and field observations exists that demonstrates that nonclassical behavior of solute transport seems to be the rule rather than the exception in fractured rocks. One of the main reasons for anomalous transport is that natural fracture networks exhibit fractal properties and can be classified as percolation media. Three physical factors affecting solute transport regimes in geologic media were singled out as the most important. These are (i) the scale-invariance properties of percolation clusters, (ii) the availability of traps related to the low-permeability matrix and dead ends of fracture clusters, and (iii) the presence of strong spatial and temporal fluctuations in the fluid flow characteristics. Theoretical and numerical approaches should provide a description of solute transport regimes in space and time, including the structure of concentration tails.

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