Solute transport in a single fracture with negligible matrix permeability: 1. fundamental mechanisms

J. Bodin · F. Delay · G. de Marsily

Abstract This report describes the fracture-scale mechanisms acting on solute transport in fractured aquifers under natural-flow conditions. It focuses on low-permeability rocks where advection in the matrix is negligible compared with that in fractures. The relevant transport mechanisms detailed have been identified by experimental and theoretical studies over the past 30 years: advection and hydrodynamic dispersion, channeling effects, matrix diffusion, and sorption reactions. This review is intended to emphasize the fundamental concepts and to draw up a reader's guide through an extensive bibliography by linking key problems to key papers. These concepts might be integrated into transport models, but their influence at the large scale, however, remains an open question that is not dealt with in this review.

Résumé Ce rapport décrit les mécanismes agissant sur le transport de soluté dans les aquifères fissurés en régime d'écoulement naturel. L'accent est mis sur les roches peu perméables, où le transport par convection dans la matrice est négligeable devant la convection dans les fractures. Les mécanismes de transport sont analysés à l'échelle de la fracture: convection et dispersion hydrodynamique, chenalisation, diffusion dans la matrice et réactions de sorption. L'objectif de ce travail est double: d'une part, mettre en avant les concepts fondamentaux pouvant être intégrés dans les modèles de transport, et d'autre part, établir un "guide" permettant au lecteur de s'orienter à travers une bibliographie abondante, en reliant chaque sujet abordé à quelques articles clés. Notons que l'influence de ces mécanismes sur le transport à grande échelle reste un problème clé qui ne sera pas abordé ici.

Resumen Este informe describe los mecanismos que actúan a escala de fractura en el transporte de solutos en acuíferos fracturados, bajo condiciones de flujo natural. Se centra en rocas de baja permeabilidad en las que la advección en la matriz es despreciable en relación con la advección en las fracturas. Los mecanismos de transporte relevantes han sido identificados mediante estudios experimentales y teóricos realizados en los últimos 30 años. Consisten en advección y dispersión hidrodinámica, influencia de los canales, difusión en la matriz y reacciones de sorción. Esta revisión pretende enfatizar en los conceptos fundamentales y generar una guía para el lector por medio de una bibliografía abundante que relaciona los problemas clave con artículos clave. Estos conceptos podrían ser integrados en modelos de transporte, pero su influencia a gran escala es todavía un tema no resuelto, el cual no se aborda en este trabajo.

Keywords Conceptual models · Fractured rocks · Solute transport · Topical review

Received: 21 August 2002 / Accepted: 4 April 2003
Published online: 24 June 2003

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Introduction

The problem of solute transport in fractured media has become a major research area in hydrogeology over the last two decades. Two fundamental worldwide issues are directly concerned: the selection of repository sites for radioactive waste in deep geological formations, and groundwater pollution in fractured reservoirs. Despite 30 or so years of effort, a model enabling the accurate simulation of pollution migration in a fractured aquifer at the regional scale is still to be designed.

This article is the first part of a review dedicated to solute transport in fractured aquifers at the fracture scale. The aim is to propose a basic guideline through the abundant literature for applied hydrogeologists and young researchers who are not necessarily knowledgeable about fractured media and advanced modeling concepts. The focus will be on current knowledge about transport mechanisms at the fracture scale and the link between key

 DOI 10.1007/s10040-003-0268-2

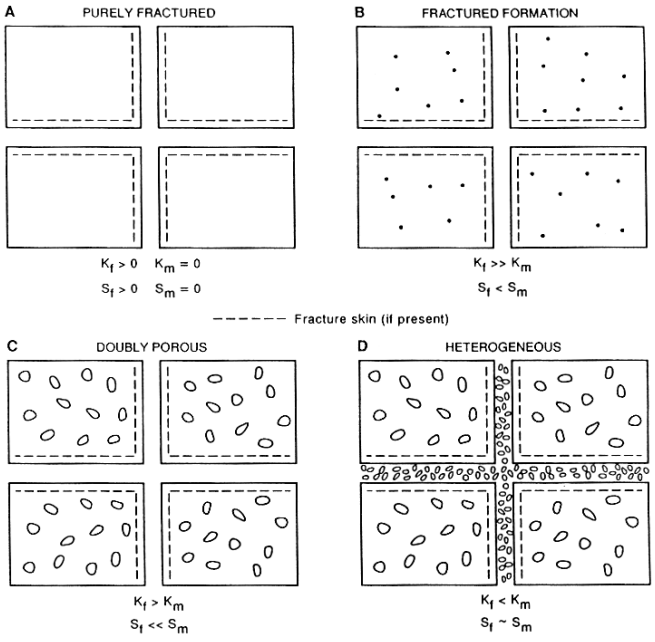

Fig. 1 Categorization of rock-soil systems where K_f, K_m, S_f and S_m, represent the hydraulic conductivities and storage coefficients of the fractures (*f*) and the matrix (*m*). Reprinted from Journal of Contaminant Hydrology, vol. 31, Robinson NI, Sharp JM, Kreisel I, Contaminant transport in sets of parallel finite fractures with fracture skins, pp. 83–109, Copyright (1998), with permission from Elsevier Science

problems and key papers. Other general or focused reviews have been published in the past, dealing with both flow and transport in natural and synthetic fractured media (Bear et al. 1993; Sahimi 1993, 1995; National Research Council 1996; Adler and Thovert 1999; Faybishenko et al. 2000), and with more specific issues such as the transport of radionuclides in fractured rocks (Williams 1996), or with flow and transport in unsaturated fractured media (Pruess et al. 1999; Faybishenko et al. 2000). Referring to the classification of fractured rocks suggested by Streltsova (1976) and followed by Robinson et al. (1998), in Fig. 1, the present review is specifically dedicated to the case of "purely fractured rocks" and "fractured formations", where the permeability of the rock matrix is negligible compared with that of fractures. Note that the relevance of the "purely fractured rocks" concept is questionable at any scale because the effects of solute diffusion in the rock matrix are non-negligible in most cases (see the section on Matrix Diffusion). Moreover, this article only reports on single-phase flow, in the saturated zone, under steady-state conditions, and for a laminar regime. It is also assumed that the flow field is known. In specific cases, this assumption ought to be used with care because incomplete knowledge of the flow field is a source of uncertainty in predicting solute transport in natural fractures.

The physical mechanisms generally acting on solute migration in fractures have been well identified. It is known that transport is the consequence of:

- Advection of the solute at the mean-fluid velocity in the fracture plane. Advection in the matrix is negligible in most cases because of the high contrast of permeability between fractures and matrix.
- Hydrodynamic dispersion stemming from the variations of the local fluid velocities with respect to the mean velocity value,
- Diffusion of the solute in the fracture plane and in the rock matrix.
- Physico-chemical reactions between the solute and the solid material of the matrix and the fracture walls.

The various aspects of the above-mentioned mechanisms have been highlighted by experimental and theoretical studies over the last three decades. The present work emphasizes the fundamental concepts that could be integrated into transport models: advection and hydrodynamic dispersion, channeling effects, matrix diffusion, and sorption reactions. Their influence at a large scale is one of the key problems of ongoing research and is not addressed in this review. A second article will be dedicated to the basic mathematical expressions used to describe solute transport in fractures.

Heterogeneity of the Flow-Velocity Field and Hydrodynamic Dispersion

Dispersion in its widest sense describes the spatial spreading of a mass injected into a flow field, i.e., the increase in the size of the plume during transport. For a given location in space, the dispersion may also be conceived as the temporal evolution of the local concentrations because the spatial dispersion is also responsible for the spreading of the arrival times of the tracer particles. Dispersion mechanisms have a major influence on pollutant migration in an aquifer, bringing about both a dilution of concentrations and shorter first-arrival times of the solute at a given location.

In other words, mechanisms such as matrix diffusion and sorption reactions (which will be detailed later) yield dispersion in its wide sense. However, one must consider the solute spreading stemming from the heterogeneity of the fluid velocities (hydrodynamic dispersion). This heterogeneity occurs at the local scale for which the mean aperture between the fracture walls is almost constant. It develops also at the larger scale in the fracture plane when mean apertures vary significantly in space. Channeling will be discussed in a section so named and can be viewed as an amplification such that the flow is concentrated in limited regions of the fracture plane. Even if the main purpose of this paper is devoted to mechanisms at the scale of single fractures, they can be briefly discussed with the relative importance between dispersion at this scale and at the scale of an entire network. Two of the following subsections address the characterization of dispersion on the basis of tracer tests and anomalous behavior of solute spreading due to scale effects.

 DOI 10.1007/s10040-003-0268-2

Hydrodynamic Dispersion at the Local Scale (Fracture Aperture Almost Constant)

The concept of Taylor–Aris dispersion (Taylor 1953; Aris 1956, 1959; Wooding 1960; Brenner 1980; Broeck 1990) was first developed as the consequence of the parabolic profile of fluid velocities in laminar flow between two parallel plates, and of molecular diffusion in free water that enables the solute to experience different velocities. In rough fractures with laminar flow, the principle of the parabolic profile remains locally valid, even if its shape varies along the fracture plane (see following article 2, Bodin et al. 2003). Thus, the concept of dispersion, developed by Taylor–Aris, may apply to more realistic fracture representations than the parallel-plate model. In the earliest stages of transport, the Taylor–Aris dispersion is transient. Beyond a given time (or a given travel distance), the solute has experienced all the profile velocities and this results in an asymptotic behavior to the dispersion. With a non-reactive solute, this critical time is proportional to the transverse diffusion characteristic time and, thus, depends on the fracture aperture and the molecular-diffusion coefficient. For a reactive solute with sorption on the fracture surfaces, Wels et al. (1997) showed that the asymptotic Taylor–Aris dispersion is reached later. The critical time should be corrected with a retardation coefficient, leading to long time values in the case of very reactive solutes.

At the scale where the mean aperture of the fracture remains almost constant, the roughness of the fracture surfaces adds another spreading mechanism. The influence of roughness on dispersion has been studied by several authors from experimental models. Examples of such studies are given by Dronfield and Silliman (1993), who carried out tracer tests between Plexiglas plates with grains of sand or small plastic blocks glued on the surfaces, and by Ippolito et al. (1993, 1994), who compared the results of echo-tracer experiments performed between two glass plates (smooth fracture) and between a glass plate and an acid-attacked zinc plate (rough fracture). In these three studies, the tracer dispersion was systematically higher in rough fractures than in smooth ones, in which Taylor–Aris dispersion is the only effective dispersion mechanism. Ippolito et al. (1993, 1994) have shown that the effect of wall roughness does not suppress Taylor–Aris dispersion, but rather superimposes on it. Note that in the laboratory models used by Dronfield and Silliman, or by Ippolito et al., the fracture geometry is extremely simplified by comparison with the characteristics of a natural fracture. The advantage of these models is an easier control on the flow field, which allows one to focus on the influence of a specific mechanism. Some techniques also permit the study of flow and transport in more realistic geometries by making resin or molten-glass replicas of natural fractures (Glass and Nicholl 1995; Kovscek et al. 1995; Persoff and Pruess 1995; Brown et al. 1998; Detwiler et al. 1999; Wan et al. 2000; Isakov et al. 2001).

Hydrodynamic Dispersion at the Scale of the Fracture Plane (Varying Aperture)

Aperture variability in the fracture plane results in heterogeneity in fluid velocities. As a consequence, dispersion will depend on the spatial correlation of the flow field. The relationship between the geometrical characteristics of the fracture aperture and hydrodynamic dispersion has been addressed numerically by several authors (Moreno et al. 1988; Thompson and Brown 1991; Koplik et al. 1993; Amadei and Illangasekare 1994; Ewing and Jaynes 1995; Gutfraind et al. 1995; Plouraboué et al. 1998; Roux et al. 1998; Detwiler et al. 2000). As for Taylor–Aris dispersion, weak variations of the fracture aperture result in an asymptotic dispersion (Gelhar 1993). Following the stochastic-dispersion theory in heterogeneous media (Gelhar and Axness 1983), it can be calculated that dispersion is fully developed and has reached its asymptotic behavior beyond a transport distance of ten times the correlation length of the apertures. The strength of this theory has been experimentally tested by Keller et al. (1995, 1999), using laboratory tracer tests in natural fractures and X-ray imagery to follow the solute motion. The theoretical dispersivity calculated with the solution by Gelhar (1993) was about two times higher than the experimental dispersivity. According to Keller et al., this fair agreement between theory and experiments could be attributed to experimental uncertainties and/or to flow channeling that is not accounted for by the stochastic theory.

The variance of apertures, therefore, is an important parameter because it increases the contrast in the fluid velocity field (Tsang and Tsang 1989). To some extreme, the individualization of preferential flow paths (see the section on Channeling) has noticeable effects on solute dispersion (Neretnieks et al. 1982; Moreno et al. 1988; Haldeman et al. 1991; Johns and Roberts 1991; Tsang et al. 1991; Moreno and Neretnieks 1993b; Abelin et al. 1994; Amadei and Illangasekare 1994; Zimmerman and Bodvarsson 1996; Lapcevic et al. 1999). Dispersion is increased if the flow paths are almost independent and with contrasting velocities. However, the effects of aperture variations (and channeling) on dispersion may be negligible if the fluid mixing is sufficient between the flow paths (Moreno et al. 1988; Moreno and Neretnieks 1993b), or if there are "mixing zones" in the fracture plane (Rasmuson 1985). Ewing and Jaynes (1995) showed by numerical simulations that the hydrodynamic dispersion, stemming from the aperture variation, decreases with the increase of the ratio: size of the fracture plane/correlation length of the aperture field.

The hydrodynamic dispersion of a solute flowing in a natural fracture, therefore, is the consequence of the three mechanisms occurring simultaneously: Taylor–Aris dispersion, roughness dispersion, and aperture-variation dispersion. As regards non-reactive solutes, the mechanisms are almost independent and their effects add up (Ippolito et al. 1994; Detwiler et al. 2000). As regards reactive solutes, the process is more complicated because

 DOI 10.1007/s10040-003-0268-2

the dispersion mechanisms may interact (Berkowitz and Zhou 1996). The relative contribution of each mechanism to the effective hydrodynamic dispersion depends on the fluid velocity: for a given velocity value, some mechanisms are negligible whereas others are prevalent. In the case of a non-reactive solute flowing in a rough fracture and ignoring molecular diffusion that prevails for very low flow velocities, Roux et al. (1998) distinguish between two dispersion regimes. For intermediate velocities, i.e., those observed in a fracture under natural flow, the solute spreading mainly results from the aperture variations. For higher velocities, Taylor–Aris dispersion predominates.

This evolution of the dispersion regimes with fluid velocity was experimentally verified by Ippolito et al. (1994). Both physical experiments and numerical simulations performed by Detwiler et al. (2000) also confirm this theory. With a theoretical work based on the aperture distributions, Detwiler et al. (2000) developed analytical expressions for calculating the Peclet values corresponding to the transition between the different dispersion regimes. They showed theoretically and experimentally that, in some cases (i.e., for certain aperture statistics), the transition from the molecular diffusion regime to the Taylor–Aris regime could be direct, the variable aperture dispersion being concealed.

Is Dispersion in Single Fractures Negligible at the Network Scale?

At the scale of a fracture network, the wide variation of fluid velocities over all the various flow paths yields another dispersion that is superimposed on the hydrodynamic dispersion in single fractures. Some authors assert that dispersion at the scale of the network predominates and hides completely the dispersion in single fractures. Thus, the latter could be neglected in transport models (Schwartz et al. 1983; Smith and Schwartz 1984; Cacas et al. 1990a; Moreno and Neretnieks 1993b). This approach considerably simplifies the calculations, but the assumption that consists in neglecting the "microdispersion" of single fractures is questionable, particularly when dealing with pollutant transport. In fact, Kapoor and Gelhar (1994a, 1994b) show that microdispersion tends to reduce the magnitude of fluctuations of concentrations in a heterogeneous aquifer. Thus, the peaks of simulated breakthrough curves for pure advection as compared with advection-dispersion in fractures may appear to be fairly different.

Other authors also neglect dispersion in fractures in view of the effects of matrix diffusion. Here again, even if some tracer tests are satisfactorily interpreted in this way (Grisak and Pickens 1981; Maloszewski and Zuber 1992), this assumption may lead to significant errors, particularly for small flow velocities (Tang et al. 1981). Therefore, microdispersion should not be neglected when dealing with radionuclide migration from repository sites because it may significantly lower the arrival times in the biosphere. Consequently, the radioactivity level of the solute may be much higher than that predicted assuming pure advection in fractures (Rasmuson and Neretnieks 1981).

Dispersion Characterization

Whatever method is used to interpret dispersion characteristics, i.e., a tracer experiment or a numerical simulation, the solute dispersion can be analyzed using two approaches:

- From spatial moments of the solute plume at a given time.
- From the breakthrough curve (concentration versus time) at a given location.

The first approach is suitable for numerical simulations in the sense that all concentrations in space are available at a given time. Field experiments require a dense network of observation points and for obvious economical reasons such facilities are rare and are proposed only for specific experimental sites. The site studied by Lapcevic et al. (1999) is a good example. Twenty-seven boreholes are spread over less than 1,500 m^2 and dedicated to follow the tracer migration along a single horizontal fracture. The occurrence of the horizontal orientation of the fracture in this site is explained by the geological structure, alternating calcareous and shale layers with open joints between the layers. In this experiment, a horizontal joint was insulated by means of packers and the tracer test was performed under "natural" flow conditions. Observations of the tracer plume showed significant transverse dispersion because the width of the plume increased two to three times the source diameter. The discrete numerical model, designed to match the observational data, included matrix diffusion and both longitudinal and transverse hydrodynamic dispersion. Note that transverse dispersivity varied over a wide range (0.01–0.22 m).

The advantage of the plume spatial analysis is to permit characterization of the effective dispersion on the basis of the evolution of the concentration spatial moments over time. With a breakthrough curve at a given location or just a single image of the plume at a given time, dispersion is only "apparent" because the analysis assumes spatial homogeneity of the dispersion mechanisms along the travel distance (Jussel et al. 1994). The analysis of dispersion at the field scale usually requires at least two wells, i.e., one for the tracer injection and one for monitoring the breakthrough curve. Note that Novakowski et al. (1998) also propose an estimate of the transport properties in fractured or porous media with tracer experiments in a single well. The dispersion analysis from breakthrough curves is often performed by fitting an analytical solution to data. Some authors also propose methods based on the calculation of temporal moments of the solute concentrations (Rasmuson 1985;

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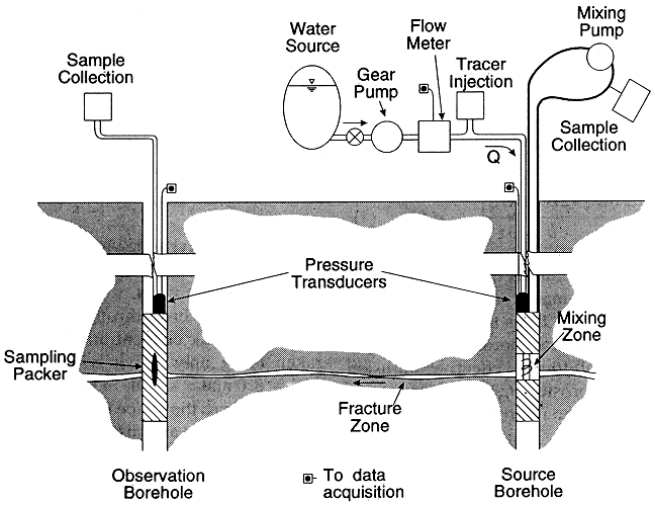

Fig. 2 Schematic diagram of the apparatus used in the tracer experiment of Novakowski (1992). Reprinted from Water Resources Research, vol. 30(1), Novakowski KS, Lapcevic PA, Field measurement of radial solute transport in fractured rock, pp. 37–44, Copyright (1994), with permission from American Geophysical Union

Harvey and Gorelick 1995; Rubin et al. 1997; Delay et al. 1998).

Field tracer tests must be designed and performed with care to avoid interference effects on the apparent dispersion (Cady et al. 1993). Many risks of potential errors are related to anomalous mixing and dilution of the tracer within the injection and observation wells. The experimental data must be corrected for a precise identification of the dispersion intrinsic to the medium (Maloszewski and Zuber 1990). Thus, Novakowski (1992) proposes a semi-analytical model for tracer tests in divergent radial flow capable of handling the dilution effects in the wells. Tsang et al. (1991) also propose two methods for the interpretation of breakthrough curves in the case of complex injections (i.e., non-instantaneous injection with varying inlet concentrations). The first method is based on fitting the model output to the first concentration peak arriving at the observation point. The second method performs a deconvolution with respect to time of the whole concentration curve.

Field tracer tests in single fractures are often carried out over short travel distances (<30 m) and fractures are isolated with packers in the boreholes. Some experimental devices are expected to minimize possible dilution effects in the wells (Novakowski et al. 1985; Raven et al. 1988; Novakowski 1992; Hadermann and Heer 1996; D'Alessandro et al. 1997). An example of an optimized setting is illustrated in Fig. 2, where the lag distance between packers is reduced, and where the measurements are directly performed within the wells. The problems of tracer dilution within the wells can also be minimized by performing experiments between two wells with injection-withdrawal (dipole) configuration, which reduces the residence time in the wells. Note also that dipole tracer tests are very convenient because they permit examination of a larger volume of rocks than with a single injection point in a convergent radial flow. Moreover, the tracer is almost completely recovered, which may become indispensable for security reasons when dealing with radioactive tracers (Andersson et al. 1993). The radioactive tracers present some advantages in certain cases because they are easy to measure in small concentrations, and specific detectors can be installed in the boreholes, which avoids the sampling operations (Robinson and Tester 1984; Raven et al. 1988; Stephenson et al. 1989).

Anomalous or Non-Fickian Dispersion

The classical theory of hydrodynamic dispersion based on the Fickian model assumes (Dagan 1989):

- Dispersion is independent of time or of the travel distance.
- For an instantaneous or short-duration source of solute, the spatial distribution of the tracer at a given time is Gaussian.

The validation of these assumptions is not always easy in fractured media because hydrodynamic dispersion seems to either increase with the travel distance (Neretnieks 1983; Abelin et al. 1991; Neuman 1990; Gelhar et al. 1992; Nordqvist et al. 1996; Lin and Lee 1998), or decrease (Tsang et al. 1991). In many cases, the spatial distribution of the tracer is complex and multimodal shapes and/or tailing effects are observed on the breakthrough curves.

An increasing dispersion with the travel distance is clearly shown in the works by Gelhar et al. (1992) and Neuman (1990), gathering numerous data from tracer tests at different scales. However, if only reliable data are selected, the long-term behavior of dispersion is hard to grasp (Gelhar et al. 1992, 1993; Neuman 1993). It is difficult to determine whether hydrodynamic dispersion keeps increasing or reaches the asymptotic behavior predicted by Gelhar and Axness' theory (Gelhar and Axness 1983). This theory stems from stochastic transport equations in heterogeneous media and shows that beyond a given travel distance, the tracer dispersion may reach the Fickian regime. However, it seems that sometimes dispersion never reaches the asymptotic limit and keeps increasing with the distance. According to Dverstorp et al. (1992) and Tsang et al. (1996), the model by Gelhar and Axness (1983) fails when the heterogeneity of the medium obeys a multi-scale organization and/or when flow channeling occurs. Studies by Schwartz et al. (1983) at the scale of fracture networks and by Plouraboué et al. (1998) or Roux et al. (1998) at the scale of single fractures with self-affine apertures seem to confirm the relationship between channeling and anomalous dispersion. The tracer follows almost independent and individualized flow paths with variable velocities from one path to the other. Thus, dispersion remains necessarily time and distance dependent.

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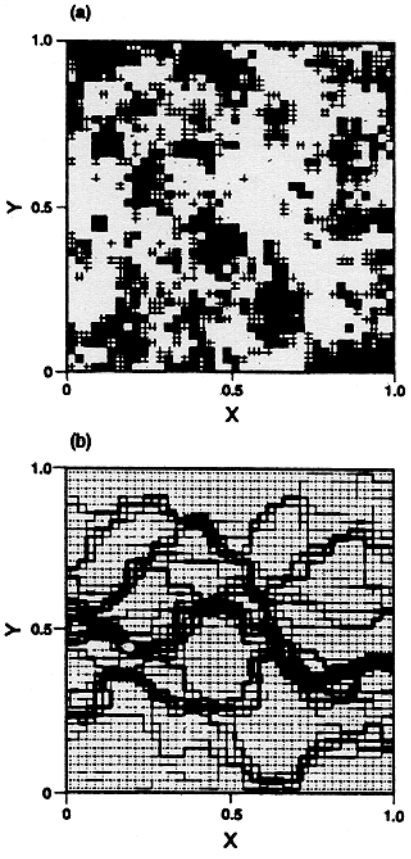

Fig. 3.a A discretized representation of apertures in a fracture plane. The magnitudes of the apertures are indicated by shading, with lighter shading corresponding to larger apertures. **b** Relative flow rates for the apertures, assuming constant-pressure boundaries on the left and right, and no-flow boundaries for the top and bottom. *Line thickness* is proportional to the square root of the flow rate. Reprinted from Water Resources Research, vol. 27(12) Tsang CF, Tsang YW, Hale FV, Analysis of field data based on a variable-aperture channel model, pp. 3095–3106, Copyright (1991), with permission from American Geophysical Union

Channeling

The channeling concept refers to preferential flow paths and may apply to both a single fracture and a fracture network. Experimental observations and theoretical studies over the last 15 years have shown that flow channeling is a common phenomenon in fractured rocks (Tsang and Neretnieks 1998). In a single fracture, channeling is related to the aperture variations in the fracture plane. The flow is concentrated along the tortuous paths with the lowest hydraulic resistance, as illustrated in Fig. 3. The channeling concept can explain some shapes of breakthrough curves at the outlet of single fractures, typically for instantaneous or short-duration injections: multimodal curves when channels are relatively independent (Moreno and Tsang 1991; Tsang 1993; Park et al. 1997), or tailing effects when small fractions of solute follow low-velocity paths (Tsang 1984; Tsang and Tsang 1987; Moreno et al. 1988; Maloszewski and Zuber 1992). Channeling in the fracture plane has been demonstrated by tracer experiments in natural fractures. A good example is described by Abelin et al. (1994) and Neretnieks (1993). It concerns the multitracer experiment at Stripa (Sweden) between two boreholes in a fracture plane. The results showed that the preferential flow channels were about 50 mm wide and corresponded only to 5–20% of the fracture plane. A detailed study of flow paths was done by Brown et al. (1998) at the laboratory scale. The authors performed steady-state flow experiments in a transparent replica of a natural rock fracture made with epoxy resin. They used video imaging and nuclear magnetic resonance Imaging (NMRI) techniques to analyze the fluid-velocity distribution within the fracture. The results show that the fluid velocities at various locations in a fracture plane can range over several orders of magnitude, but the maximum velocity is only five times higher than the mean velocity. Channeling is also revealed by computer simulations of flow and transport in fractures with variable local apertures (Brown 1987; Moreno et al. 1988; Tsang and Tsang 1989; Tsang 1993; Fig. 3). Almost any numerical model that solves fluid flow and solute transport in discrete fracture planes can simulate channeling. The only constraint is to discretize the fracture plane with a series of elements (or cells) and assign a variable aperture for each element. By choosing the aperture from a spatially correlated distribution, channeling such as shown in Fig. 3 is obtained. Examples of such models are presented by Nordqvist et al. (1992) and by Therrien and Sudicky (1996). The limitations of this approach, for large-scale simulations, are the high requirements on computer capabilities if a large number of fractures must be finely discretized, and also the lack of sufficient data to infer the aperture variability for real fractured systems.

In practice, however, the channeling concept is rarely taken into account for interpreting hydraulic or tracer tests in natural fractured media. Most of the "traditional" models consider fractures as parallel-plate systems with constant apertures (see e.g., Folger et al. 1997). Obviously, this simplification does not fully describe flow and transport in natural conditions. This is one of the reasons why the "equivalent" fracture apertures inferred from tracer tests are generally higher than those inferred from hydraulic tests (Tsang 1992; Zimmerman and Yeo 2000). A result based on the mean travel time of the tracer is sensitive to the mean aperture of channels, whereas a result based on fixed flow rates and pressure gradients is mostly influenced by small apertures with high resistance to the flow. The differences between the mean apertures inferred from both methods can be of about 20 % (Novakowski et al. 1985; Shapiro and Nicholas 1989; Silliman 1989; Cady et al. 1993; Lapcevic et al. 1999). These differences were observed both in crystalline and carbonate rocks. Knowing that the results from both flow and transport simulations are very sensitive to fracture apertures, the accuracy of solute travel times and concentrations are strongly influenced by the measurement uncertainty for this parameter (Woodbury 1997).

 DOI 10.1007/s10040-003-0268-2

Matrix Diffusion

Effects of Matrix Diffusion and Experimental Evidence

The effects of solute diffusion into the rock matrix have been neglected in the first transport models (Schwartz et al. 1983; Endo et al. 1984; Long and Witherspoon 1985), but, over the last two decades, many theoretical and experimental studies have shown the great influence of matrix diffusion on transport (Foster 1975; Freeze and Cherry 1979; Grisak and Pickens 1980; Neretnieks 1980, 1983; Bibby 1981; Maloszewski and Zuber 1985; Moreno et al. 1985; Harrison et al. 1992; Sudicky and McLaren 1992; Suksi et al. 1992; McKay et al. 1993; Wood et al. 1993; Toran et al. 1995; Hadermann and Heer 1996; Fahy 1997; Stafford et al. 1998; Lapcevic et al. 1999; Novakowski and Bogan 1999; Wendland and Himmelsbach 2002). Some authors even consider that matrix diffusion can control solute transport in a fractured rock when the matrix porosity is high (chalk, for instance; Maloszewski and Zuber 1990; Maloszewski and Zuber 1993; Zuber and Motyka 1994). In that case, the geometry of the fracture network and the hydrodynamic dispersion could play a secondary role. Guimera and Carrera (2000) studied data from 90 tracer experiments performed in low-permeability media. The data have been reexamined using simple models (homogeneous domain, steady-state flow regime, single porosity). Hydraulic conductivity was derived as the ratio: water flux/head gradient, and apparent porosity as the ratio: water velocity/water flux. The water velocity was estimated from both first- and peak-arrival times. The authors showed that the apparent porosity derived from peak-arrival time tends to increase with the square root of the travel time, whatever the flow rates. For these authors, this is consistent with the non-negligible influence of matrix diffusion in the tracer-test experiments.

Regarding transport, diffusion mainly causes a slowdown in the migration of the solute and a decrease in the concentration peaks. Of course, these effects are very important for assessing the risk of pollution in an aquifer. Sudicky and Frind (1982) have shown with analytical expressions that the travel times in systems with matrix diffusion are significantly larger than those where only transport in fractures is taken into account. The differences may reach one order of magnitude. For lower matrix porosity, as in crystalline rocks, the role of diffusion remains significant. For a travel distance of 100 m, a matrix porosity of 1% may delay the concentration peaks by half an order of magnitude in time, and lower the maximal concentrations by one order of magnitude (Novakowski and Bogan 1999).

For instantaneous or short-duration sources of solute, matrix diffusion may also lead to tailing effects on breakthrough curves as in the case with channeling (Novakowski and Lapcevic 1994; Novakowski et al. 1995; Garcia-Gutierrez et al. 1997; Sidle et al. 1998). Figure 4 shows examples of breakthrough curves with very flat tails resulting from matrix diffusion. This

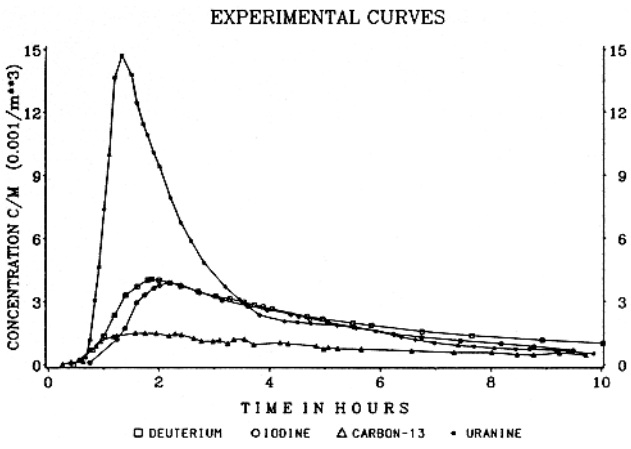

Fig. 4 Tracer-concentration curves in a multitracer experiment conducted in a chalk formation (original data adapted from Garnier et al. 1985). Reprinted from Water Resources Research, vol. 26(7), Maloszewski P, Zuber A, Mathematical modeling of tracer behavior in short-term experiments in fissured rocks, pp. 1517–1528, Copyright (1990), with permission from American Geophysical Union

feature, which is common to both channeling and matrix diffusion, emphasizes possible problems in the interpretation of tracer experiments because it can be hard to determine which mechanism is represented by the observed tail. Maloszewski and Zuber (1990) state that multi-tracer tests should be used to distinguish between both processes. Diffusion properties (and therefore the matrix-diffusion process) may vary from one tracer to the other because of the molecule size, whereas channeling remains unchanged. Maloszewski and Zuber argue to that end, using the results of a multi-tracer experiment in fractured chalk carried out by Garnier et al. (1985). The clear differences in the breakthrough curves (Fig. 4) are interpreted as the consequence of a dominant matrix diffusion that varies according to the different tracers. Other recent studies have shown the interest in using several tracers with contrasting diffusion coefficients. Jardine et al. (1999) performed a long-term (550 days) tracer experiment in fractured shales under natural flow conditions and quantified the diffusive flux between fractures and the matrix from a comparison between the breakthrough curves. Callahan et al. (2000) carried out two types of tracer tests in fractured tuff cores. In the first type, sodium iodide (NaI) was injected in separate experiments at different flow rates. In the second type, two tracers with different diffusion coefficients were injected. The authors showed that the processes of matrix diffusion and dispersion within the fracture could be effectively separated by interpreting simultaneously the results from both methods.

Becker and Shapiro (2000) give a counter example where matrix diffusion is of weak influence on transport. They interpret the results of a field-scale multitracer experiment performed in crystalline rocks, at the Mirror Lake site, central New Hampshire, USA. The tracer tests were conducted between boreholes separated by 35 m.

 DOI 10.1007/s10040-003-0268-2

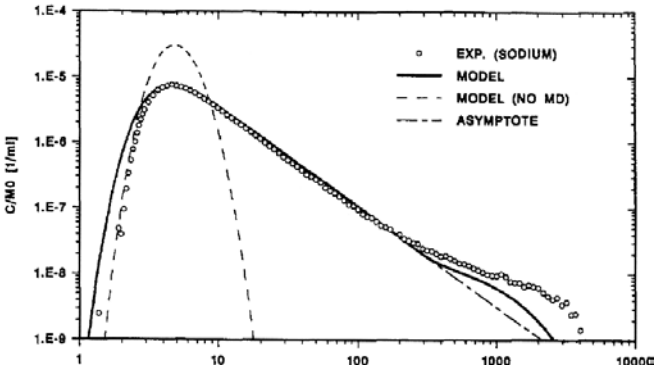

Fig. 5 Experimental breakthrough curve (*circles*) and model fit (*full line*) of a sodium tracer experiment at the Grimsel (Switzerland) test site. The *dashed line* represents transport modeling without matrix diffusion (MD). The *dashed-dot line* shows the asymptotic analytical solution for the dual-porosity model with a $t^{-3/2}$ dependency of the concentrations. Reprinted from Journal of Contaminant Hydrology vol. 21, Hadermann J, Heer W, The Grimsel (Switzerland) migration experiment: integrating field experiments, laboratory investigations and modelling, pp. 87–100, Copyright (1996), with permission from Elsevier Science

The extended breakthrough tailing is consistent for all the tracers despite a wide range in molecular diffusivity. This behavior, thus, is attributed by the authors to advection-dominated transport processes. In another study at the Mirror Lake site, Shapiro (2001) interpreted the relationships between tritium (H^3) and dichloro-difluoromethane (CFC-12) concentrations in groundwater samples collected over a 4-km^2 area. This investigation showed that the effects of solute diffusion into the rock matrix were small compared with mass exchanges by advection between fractures of high and low permeability. As stated in the Introduction, these results point out the notion that the scale of the system in which a transport process occurs has some importance in defining solute transport scenarios.

According to Tsang (1995), single-well injection/recovery tracer tests are also efficient for assessing the influence of matrix diffusion because the effects of channeling are strongly reduced by the inversion of the flow field. However, Lessof and Konikow (1997) have shown that, by numerical simulations, the regional ground-water flow (drift) sometimes yields to an irreversibility of the advective motion of the solute plume. Thus, the tracer-recovery curves may yield a wrong interpretation regarding the possible occurrence of matrix diffusion. Multiple trials of various configurations, therefore, is a good way to reduce the uncertainties in the identification of transport mechanisms (Callahan et al. 2000). In the same way, for dipole configurations (one injection well and one pumping well), Kunstmann et al. (1997) have shown the benefit of two successive tracer tests with an inversion in the roles of the wells.

Other indicators are helpful for interpreting the tailing of the breakthrough curves. A concentration proportional to $t^{-3/2}$, easily visible on a log–log plot as in Fig. 5, confirms the occurrence of diffusive fluxes between fractures and the matrix (Hadermann and Heer 1996).

Laboratory Diffusion Experiments

The diffusion properties of a solute into a rock are often characterized by laboratory experiments on rock samples of centimetric size subjected to concentration gradients (through diffusion experiments; Feenstra et al. 1984; Bradbury and Green 1985, 1986; Skagius and Neretnieks 1986b; Siitari-Kauppi et al. 1994; Yamaguchi et al. 1997; Byegard et al. 1998; Johansson et al. 1998; Yamaguchi and Nakayama 1998; Moridis 1999; Sato 1999; Callahan et al. 2000; Tidwell et al. 2000; Boving and Grathwohl 2001). Tidwell et al. (2000) used X-ray absorption imaging to study the transient motion of the tracers. This technique allows one to measure the 2-D relative concentration distribution in the samples at different times during the experiment. The authors showed that the spatial variations in the diffusion coefficient were directly related to the heterogeneous porosity characteristics of the samples. Johansson et al. (1998) studied, successively, the diffusion properties of several radionuclides in crystalline-rock samples by through-diffusion experiments, and the porosity distribution of the rock samples using the ^{14}C-polymethyl-methacrylate (PMMA) impregnation method (Hellmuth et al. 1993). They showed that the radionuclide diffusion in the rock matrix follows a double-porosity network of slow and fast migration pathways. The authors conclude that the assumption of a homogeneous matrix, commonly used for interpreting diffusion experiments, can lead to substantial errors. Another way to characterize the diffusion properties of a solute into a rock is to proceed to in- or out-diffusion experiments. With this method, the rock samples are saturated with a tracer solution (or clean water), and immersed into a container filled with clean water (or tracer solution). The diffusion coefficients are calculated on the basis of concentration changes in the container (Moridis 1999). Examples of such experiments are reported by Hölttä et al. (2001) and Xu and Wörman (1999), who used cubic rock samples of centimetric size, and by Novakowski and van der Kamp (1996) who developed a model for interpreting radial diffusion from or into core-sized samples. Ibaraki (2001) proposed also a simplification of the in-diffusion method for monitoring the concentration into the container by electrical conductivity measurements. Tracer tests can also be carried out in laboratory columns of fractured rocks and interpreted with transport models that take matrix diffusion into account (Grisak et al. 1980; Hölttä et al. 1992; Reedy et al. 1996; Jorgensen et al. 1998; Sato 1999; Callahan et al. 2000).

It should be noted that most of the experiments reported in the literature were performed on crystalline rock cores extracted from potential repository areas such as the Swedish sites of Stripa and Äspö. Several data compilations (Brandberg and Skagius 1991; Neretnieks 1993; Ohlsson and Neretnieks 1995, 1997) give the orders of magnitude of the diffusion parameters in crystalline rocks. There are fewer laboratory experiments on sedimentary rocks. Examples can be found however in

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Boving and Grathwohl (2001), Haldeman et al. (1991), and Wendland and Himmelsbach (2002). Also, at the laboratory scale, Wan et al. (1996) suggest the study of exchange mechanisms between fractures and the matrix using synthetic media. Their experimental models employ chemical attacks of glass plates with hydrofluoric acid (HF). The first step consists in building the pore network and fractures are etched during a second attack. For each step, the portions of glass plates that need to remain unetched are protected by coatings. The advantage of working with this kind of model is the perfect knowledge of the medium geometry, whether it be at the fracture network level or at the pore-space level.

Because the diffusion process is slow, the main drawback of the experiments is their long duration. To speed up the measurements, Autio et al. (1998) propose the use of He gas instead of solute for through-diffusion experiments. The time required for a complete experiment with rock samples of 60–mm thickness is less than two days. The He-gas method also allows the measurement of hydraulic conductivity of very low-permeability rock samples. Skagius and Neretnieks (1986a) suggest also an interesting technique for a quick determination of the diffusion parameters of a rock. This method is based on the measurement of the electrical conductivity of rock samples saturated with a saline solution. Using this technique, Bradbury and Green (1986) were able to measure the diffusive properties of granite samples 125 cm long. Ongoing work for applying this technique to field-scale studies is done by electrical resistivity logging in boreholes (Ohlsson et al. 2001).

Relevance of Laboratory Measurements to the Field Scale

In order to evaluate in situ the diffusive properties of rocks and compare them with laboratory results obtained on small samples, an experiment was set up in the Stripa mine at a depth of 360 m (Birgersson and Neretnieks 1990). Several conservative tracers were injected into the granite over three periods of increasing length: 3 months, 6 months, and 3.5 years. The results show that the parameters defined at the laboratory scale should be interpreted with care. First, the diffusive properties of rocks in situ, which are under natural physical constraints, can be lower than those of laboratory samples by a factor of 2–2.5 (Bradbury and Green 1986; Skagius and Neretnieks 1986a). Diffusion experiments performed at the laboratory scale are thus strongly improved by applying stresses close to those that occur naturally (e.g., Rebour et al. 1997). Second, through-diffusion experiments may overestimate the pore connectivity by a factor of two if the samples are thin (<5 cm), because dead-end pores have been artificially transformed into connected ones by the slicing (Bradbury and Green 1986). Finally, the measurements performed on laboratory samples may address local properties that are heterogeneous at the field scale. Several studies performed at Stripa and Äspö showed that diffusive properties of crystalline rocks could vary by one order of magnitude over very small distances (a few tens of centimeters; Neretnieks 1993; Ohlsson and Neretnieks 1995; Xu et al. 2001).

Factors of Influence to Matrix Diffusion

Many factors related to the matrix porosity influence diffusion: connected pore volume, tortuosity, and constrictivity. Consequently, the diffusive properties of a rock will depend partly on its petrographic structure and the alteration degree of the minerals. Bradbury and Green (1986) carried out diffusion experiments on pieces of granite sampled at the altered walls of a fracture and at different distances from these surfaces. They revealed that the alteration of a rock could increase its diffusive properties by a factor ranging from 20–200. Similar results were also obtained by Siitari-Kauppi et al. (1994, 1997) and Hölttä et al. (1996), who performed diffusion experiments on crystalline rocks that had been altered to different degrees. Thin coatings of precipitated materials are often deposited on the fracture walls. Their influence on diffusive exchanges seems to be weak (Ohlsson and Neretnieks 1995). On the other hand, the diffusive fluxes are strongly influenced by the real fractured rock surface in contact with the fluid (Neretnieks 1980; Moreno and Neretnieks 1993a; Wels et al. 1996; Grenier et al. 1998). Channeling in the fracture plane, therefore, has an influence on diffusion mechanisms because it tends to reduce the effective contact surface between the solute and the matrix (Moreno et al. 1988). Actually, because of channeling in the fracture plane, the diffusion system can be separated into three compartments: exchanges between channels and the matrix, between channels and stagnant water zones in the fracture plane, and between stagnant water zones and the matrix (Rasmuson and Neretnieks 1986; Dykhuizen 1992; Grenier et al. 1998; Johns and Roberts 1991). The sensitivity analysis performed on tracer tests (Kunstmann et al. 1997), or from theoretical models (Grenier et al. 1998), showed that the solute diffusion between stagnant water zones and matrix blocks is non-negligible. Gylling et al. (1998) present a method to estimate the mean "flow wetted surface" with the linear frequency of flowing fractures in a well. Assuming that the flow channels are randomly distributed in the rock volume, the authors develop an expression that relates the number of channels in a given volume to the probability that channels are intersected by a borehole. If the length and width of the channels are large relative to the borehole diameter, the flow-wetted surface area may be determined only as a function of the average lag distance between flowing features observed in the well. Otherwise, the length or the width of the channels must be estimated from observations in galleries.

Although unlimited diffusion is often assumed in models, it remains difficult to specify the rock volumes in which the diffusion process occurs. It is known that the porosity of igneous or metamorphic rocks is in the range 1–7% in the vicinity of the fracture walls (Abelin et al.

 DOI 10.1007/s10040-003-0268-2

1991), but these values may strongly diminish with depth into the rock matrix, giving porosity values often below 0.5% in the case of unaltered rocks (Bradbury and Green 1986; Skagius and Neretnieks 1986b). The question is whether the whole matrix really participates in diffusion, or whether the mechanism is limited to the microfractured damaged zone near the fracture surfaces (Smith et al. 1997). Regarding the shales studied by Mazurek et al. (1996), the depth to which diffusion occurs seems to be about 10 cm. This value is consistent with that found by Heath et al. (1992) in Spanish granites and by Landström and Tullborg (2001) in quartz monzodiorite from Äspö (Sweden): the diffusion of natural radionuclides seems to be limited to the altered zone, corresponding to a depth of 3–10 cm on either side of the fractures. The interpretation by Ohlsson and Neretnieks (1995) of data from the literature on diffusion in igneous and metamorphic rocks confirms that diffusion occurs to a relatively small depth into the matrix. In-situ diffusion experiments suggest that even for connected matrix porosity to a depth of over 1 m, matrix diffusion remains confined to zones of highest porosity, i.e., a few centimeters into the matrix blocks bounding the fracture. In the Stripa diffusion experiment in Sweden, the distances diffused into the matrix by conservative tracers injected for 3.5 years are of about 40 cm. In a review of literature on natural analogue studies by Smellie and Karlsson (1999), the greatest depths of penetration into crystalline rocks (deduced from natural uranium decay series measurements) range from 1 mm–5 cm, although values up to 50 cm also have been observed. One could expect a larger depth of penetration for diffusion into the matrix of sedimentary rocks like sandstone or limestone, which can have matrix porosities reaching 10–20%.

Finally, Ohlsson and Neretnieks (1995) propose two concepts dealing with diffusion mechanisms in the matrix. The first one is called “surface diffusion” and applies to cations resident in a sorbed but mobile phase along the intergranular boundaries. This mechanism might increase the extent of diffusion of solutes such as sodium, strontium, and cesium by one or two orders of magnitude (Yamaguchi et al. 1993; Ohlsson and Neretnieks 1998; Xu and Wörman 1999). Therefore, it is important to take this mechanism into account, particularly for safety assessment studies. The second concept developed by Ohlsson and Neretnieks (1995) is called “anionic exclusion”. The idea is that negatively charged species might not access all the matrix porosity because of electrostatic repulsive forces, due to the occurrence of negatively charged pore surfaces. This mechanism is well observed and reported by Yu and Neretnieks (1997).

Sorption Reactions

In several cases, transport can be strongly affected by interactions between the solute and the rock minerals. Various kinds of mechanisms may be involved (Skagius 1986; Weber et al. 1991):

- Electrostatic interactions, generally between negatively charged mineral surfaces and cationic species in solution.
- Electromagnetic interactions (Van der Wall’s forces).
- Chemical interactions, i.e., chemical bonds between the solute and the grain surface.

Apart from dissolution/precipitation reactions, most of these interactions are generally referred to as sorption reactions (Freeze and Cherry 1979), and are considered as instantaneous (i.e., fast enough not to be influenced by the solute-migration velocity) and reversible processes. However, in some cases, these assumptions are not valid: kinetic effects are sometimes observed (Xu and Wörman 1999) and significant differences may occur between sorption and desorption processes, resulting in quasi-irreversible reactions or very slow desorption kinetics (Byegard et al. 1998). These phenomena are observed for instance with very reactive cations such as Cs^+, Ba^{2+}, and Rb^+.

In connection with the diffusion process, sorption reactions play a part in the slowdown and retention of solutes in geological formations. Consequently, it is important to distinguish between both processes. It must be noted that most radionuclides that could be stored in repository sites are subject to sorption on crystalline rocks (Cvetkovic et al. 1999). Because matrix diffusion is a relatively slow mechanism, solute sorption mainly occurs at the fracture surfaces when flow is fast. Conversely, for significant mean-residence times, sorption reactions mainly occur within the matrix because the available exchange surfaces in the matrix are much more important than those in the fracture. In reviewing literature on natural analogue studies, Smellie and Karlsson (1999) pointed out the strong influence of fracture coatings made of clay minerals, calcite, or Fe-oxyhydroxides on the retardation properties of fractured rocks. According to these authors, the presence of clay coatings on fracture surfaces may be more common than reported. When drilling rocks, these friable materials are easily flushed out by the water under pressure. Clay minerals in fractured crystalline rocks can be considered as stable since their formation/alteration are relatively slow geological processes. On the contrary, the retardation processes due to the presence of calcite coatings may be more difficult to handle since in active hydraulic systems, rapid processes of precipitation/dissolution may lead to significant spatial redistribution of this mineral.

The experimental method commonly used to characterize the sorption properties of a rock is the batch technique. It consists in generating an equilibrium condition between a solution of known initial concentration and crushed rocks, and in calculating the fraction of mass adsorbed at the grain surface. A detailed description of the experiment protocol is given by Wels et al. (1996). However, sorption parameters inferred from these experiments should be evaluated with care because rock crushing can increase the specific surface available for solute sorption. This was clearly demonstrated by Bye-

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gard et al. (1998), who used the BET technique, based on gas-sorption experiments at low temperature (Brunauer et al. 1938), to measure the surface area of the crushed material. These authors showed that sorption coefficients inferred from batch experiments were overestimated by one order of magnitude. Thus, their advice is to make these measurements through diffusion experiments for a better evaluation. Another method consists in setting up tracer tests within ideal fractures made of sawed and polished rock plates, and in interpreting the results with analytical solutions accounting for sorption reactions both at the fracture surface and in the matrix (Wels et al. 1996; Hölttä et al. 1997, 2001). Hölttä et al. (2001) studied with this method the sorption of sodium, calcium, and strontium on different crystalline rocks from western Finland. The sorption coefficients obtained from fracture-column experiments are one order of magnitude lower than those previously obtained from batch experiments (Hölttä et al. 1998).

Vandergraaf et al. (1996) report also an interesting migration experiment performed in a quarried block of granite of metric size containing a single, natural fracture. Several weakly and strongly sorbing radioactive tracers were injected into the fracture under steady-state flow. The block was separated along the fracture after completion of the migration experiment, i.e., one month after the radionuclide concentrations at the outlet are below the detection levels. Both fracture surfaces were scanned to study the spatial distribution of the radionuclides irreversibly sorbed on the fracture walls. The results showed a clear association of the sorbed species with specific mineral groups. As shown experimentally (Vandergraaf et al. 1997; Byegard et al. 1998), sorption properties of a rock may vary with the degree of mineral alteration. Unfortunately, results diverge and there is no clear trend between the alteration degree of a rock and its sorption capacity. The sorption properties of an altered rock mainly depend on the nature of the alteration minerals. For Byegard et al. (1998), who studied Äspö diorite and fine-grained granite in Sweden, sorption seems to be stronger for the rock samples with a large amount of biotite. The sorption seems to decrease with the degree of alteration, as the biotite is transformed into chlorite. On the other hand, Vandergraaf et al. (1997) have found stronger sorption on alteration minerals (illite and kaolinite) than on the fresh granite. Sorption reactions can also be affected strongly by other factors related to the fluid, such as pH and Eh conditions, and complexing agents able to modify the chemical characteristics of the elements in solution (Neretnieks 1993). The orders of magnitude for values of sorption parameters of different solutes on different rocks are available in several data compilations (see e.g., Ohlsson and Neretnieks 1995; Carbol and Engkvist 1997).

Conclusions

In this review, an attempt has been made to describe the major mechanisms playing a part in solute transport in a single fracture: advection and hydrodynamic dispersion, channeling effects, matrix diffusion, and sorption reactions. It is believed that several concepts might be integrated in the development of further numerical models.

The first point concerns channeling in the plane of single fractures. Indeed, this mechanism strongly affects solute transport in two ways.

1. It acts on matrix diffusion, the exchanges develop in a triple system of interfaces: channels ↔ matrix, channels ↔ stagnant water zones, stagnant water zones ↔ matrix.
2. Channeling also acts on dispersion with the potential development of anomalous behaviors.

Consequently, should a single fracture be considered as the proper basic unit to describe flow and transport in fractured reservoirs with a discrete approach? Cacas et al. (1990a, 1990b), Dershowitz and Fidelibus (1999), Gylling et al. (1999), and Moreno and Neretnieks (1993b) prefer to deal with networks of channels associated with fractures. Even if this approach strongly simplifies the local calculations, i.e., they are performed in 1–D, the channel network is always much more complex than the fracture network. This complexity may become too formidable when modeling problems at the regional scale. A second possible approach might keep the initial fracture network and artificially include the channeling effects into the transport parameters. For instance, instead of a constant dispersion coefficient (as often assumed), a parameter varying with the migration distance might be used. This approach would permit simulation of the transient behavior of dispersion before it converges towards the asymptotic Fickian regime [see section on Hydrodynamic Dispersion at the Local Scale (Fracture Aperture almost Constant)]. Berkowitz and Scher (1995) showed, however, that the use of a scale- or a time-dependent dispersion coefficient in the context of conventional transport equations is mathematically incorrect, and contradicts the fundamental assumptions used to develop these equations.

The second point is connected to the diffusion mechanisms. It would be advisable to weaken the assumption of an infinite matrix that overestimates the retardation of the tracer. The triple system of diffusion cited above could also be introduced into the numerical models. The concepts of surface diffusion and anionic exclusion (see section on Matrix Diffusion) are interesting, but their relative significance in solute transport at the scale of the network remains to be specified.

As a third point, it seems that models should be able to simulate the sorption—desorption effects with varying kinetics according to the nature of the solute.

 DOI 10.1007/s10040-003-0268-2

Acknowledgements This work was partly funded by the "Programme National de Recherche en Hydrologie" (PNRH). We are grateful to Dr. R. Therrien and Dr. W.S. Dershowitz for their constructive comments on the manuscript. We are also grateful to M.C. Ferré (UMR 6532 Hydrasa, Université de Poitiers) for helping us in seeking reprints of the references cited in this article.

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