Determination of Diffusion Characteristics of the Rock Mass

Kai Witthüser*, Dalinaidu Arnepalli† and Devendra N. Singh‡

Introduction

The pathways for contamination of the rock mass are surface or underground (domestic or industrial) waste disposals, leakage of contaminated water from e.g. sewage systems, other aquifers or for example by injection of liquid waste into wells. Whatever may be the causes for contamination of the rock mass, the transport of contaminants in the rock mass is quite different from that in porous aquifers. Contaminant transport in fractured rocks occurs in the fracture network and the porous rock blocks. Within the fracture network, through 0.1 to 5% of the total rock volume, advection occurs at higher flow velocities than within the undisturbed rock matrix.

While the interconnected fractures are therefore the dominant transport routes in a rock mass, the rock matrix, with porosities up to 50% (for some sedimentary rocks) provide a relatively large storage volume for contaminants. Due to the low permeability of the rock matrix, the dominant transport process in the rock matrix itself is diffusion, rather than advection. In other words, transport in the fracture network is driven by pressure gradients, whereas transport in the matrix is driven by concentration gradients.

The advective-dispersive transport of contaminants through a fracture network is subject to more or less continuous interactions with the bounding matrix blocks, where the uptake, release and transport of solutes is controlled

*   Department of Geology, University of Bonn, Nussallee 8, 53115 BONN, Germany. E-mail: witthueser@uni-bonn.de

†   Research Scholar, Department of Civil Engineering, Indian Institute of Technology, Bombay, Powai, Mumbai – 400076, India. E-mail: P2dali@civil iitb.ac.in

‡   Professor, Department of Civil Engineering, Indian Institute of Technology, Bombay, Powai, Mumbai – 400076, India. E-mail: dns@civil.iitb.ac.in

by the matrix diffusion. The diffusive exchange between the mobile water in the fracture and the relatively immobile pore water held in the rock matrix leads to a significant retardation of contaminant movement as well as to a reduction of the observed peak concentrations. This diffusion controlled barrier function of the rock matrix and its importance is well known from risk analyses for nuclear and underground waste deposits. Most of these studies incorporate diffusion of radioactive substances in the tested crystalline host rocks (Bigersson and Neretnieks, 1990; Lever and Bradbury, 1985; Neretnieks, 1980) as a retardation factor.

Nevertheless, unless any degradation by radioactive or microbiological decay occurs, the contaminants are only "stored" in the matrix and will be released once the concentration gradient between fracture and matrix water reverses. This effect is well known from tracer tests in fractured rocks, where a distinguished tailing of breakthrough curves is observed (Maloszewski, 1994; Lever et al., 1985; Neretnieks, 1980). Furthermore, such back-diffusion controls the slow, diffusion-limited removal rates of remediation techniques in the fractured rock mass.

Beside sorption, matrix diffusion is the primary retardation mechanism for contaminant transport in fractured rock (Lever and Bradbury, 1985). Whenever contaminant transport in the fractured rock is to be described or predicted, the effects of matrix diffusion have to be incorporated and quantified, thus the diffusion properties of a rock have to be determined. With this in view, an attempt has been made in this paper to present an overview of the basic principles of matrix diffusion and to describe an efficient experimental methodology, which can be employed for determining the diffusion characteristics of the rock mass.

Basic Diffusion Equation

In general, molecular diffusion describes the net mass transfer by random molecular motion due to concentration gradient(s) of diffusing substance(s) (Crank, 1957). According to Fick's 1st law, 1-Dimensional diffusive flux, J_d, of a solute in water due to the concentration gradient, c, is as follows:

$$J_d = -D_m \frac{\partial c}{\partial x}$$

(1)

where D_m is the free-water diffusion coefficient and x is the distance.

Diffusive transport of the contaminant in the porous rock matrix exhibits several types interactions between the matrix, the water molecules and the

solute. The reduced mobility of the contaminant in the pore water of a rock matrix, under the influence of physical interaction with the matrix and the geometrical constraints like constricted (constrictivity factor defined as δ), elongated and tortuous (tortuosity factor defined as τ) flow paths can be described by the pore diffusion coefficient, D_p:

$$D_p = D_m \frac{\delta}{\tau} \tag{2}$$

The tortuosity factor, τ, is defined as (Carman, 1956):

$$\tau = \left(\frac{L_e}{L}\right)^2 \tag{3}$$

where L_e is the actual length of the flow path and L is the length of the straight flow path in a theoretical capillary bundle. The mobility of a solute in a saturated porous media is further reduced by the available volume, i.e. the effective or transport porosity, η_e, of the media. It is described by the effective or stationary diffusion coefficient of a porous media (Grathwohl, 1998):

$$D_e = D_p \eta_e = D_m \eta_e \frac{\delta}{\tau} = D_m D' \tag{4}$$

where D_e is the effective diffusion coefficient and D' is the relative diffusivity, which describe the diffusive properties of the rock mass.

As some pores in the matrix are "dead end pores" (Lever et al., 1985) or too small in diameter to contribute to the diffusive flux, the effective or transport porosity, η_e, is usually smaller than the total accessible porosity, η. The effective porosity, the empirical constrictivity and the tortuosity factors can be summarized to the relative diffusivity, D', which describes the diffusive properties of a porous rock mass itself. The relation between different diffusion coefficients is given by:

$$D_e < D_p < D_m \tag{5}$$

1-Dimensional stationary diffusive mass flux, J_d, of a solute in a porous saturated media follows the following relationship:

$$J_d = -D_e \frac{\partial c}{\partial x} = -D_m D' \frac{\partial c}{\partial x} \tag{6}$$

Since sorption only prolongs the transient or instationary phase (Fig.2) of diffusion in a porous media, Fick's 1st law is also valid for the solutes that exhibit sorption. However, Fick's 2nd law describes the instationary diffusive transport of a sorbing or non-sorbing solute in the porous media:

$$\left(\underbrace{\eta+\rho K_d}_{\alpha}\right)\frac{\partial c}{\partial t} = D_e\frac{\partial^2 c}{\partial x^2} \tag{7}$$

where ρ is the bulk density and K_d is the distribution coefficient of a linear sorption isotherm (Henry, 1922). The term in parentheses is termed as the rock capacity factor, α, which describes the capacity of the porous media for holding a solute. For non-sorbing substances, the rock capacity factor equals the total accessible porosity.

Hence, defining the apparent diffusivity, D_a, as:

$$D_a = \frac{D_e}{\alpha} = D_p \tag{8}$$

leads to the following expression for Fick's 2nd law:

$$\frac{\partial c}{\partial t} = D_a\frac{\partial^2 c}{\partial x^2} \tag{9}$$

Experimental Determination of the Diffusion Characteristics

There are two methods of determining diffusion characteristics of the rock mass: In-situ investigations that employ tracer techniques (Käss, 1998) or laboratory experiments on samples of the rock mass, as discussed in the following sections. Determination of diffusion coefficient in natural fractures, with the help of tracers, is an extremely costly and time-consuming exercise and requires sophisticated injection and detection systems (Becker and Shapiro, 2000). In such a situation, laboratory experiments are found to be the best alternative to determine the diffusion coefficient of the rock mass. Furthermore, efforts must be made to develop an appropriate mathematical model of these experiments. For these reasons diffusion coefficient, determined by conducting tracer tests, often, are not as reproducible as those determined by conducting laboratory experiments. Nevertheless, only field investigations can verify if laboratory results are representative of the investigated part of the aquifer.

Laboratory experiments are usually performed as in-/out- or through-diffusion experiments. In in-diffusion experiments (Skagius and Neretnieks, 1988), the diffusive flux is observed from a reservoir of high solute concentration into a porous rock sample (with a known initial solute concentration, which is usually maintained at zero) or the distance that a contaminant has diffused into the rock sample from a reservoir of constant concentration is observed. In out-diffusion experiments (Tits et al., 2003), the reverse process is observed, i.e. the diffusive flux from a rock sample with initially known solute concentration is observed. However, either of these tests would yield only the apparent diffusion coefficient by describing the concentration development in the reservoir with an appropriate solution of Fick's 2nd law (Crank, 1975). In through-diffusion experiments (Feenstra et al., 1984) the diffusive flux is observed between a reservoir cell with high concentration across a porous rock sample and a receiving cell with an initial concentration of zero. The analytical solution of Fick's 2nd law for through-diffusion experiments, outlined below, yields the effective diffusion coefficient and the rock capacity factor of a rock sample, and hence also the apparent diffusion coefficient (using Eqn.8). It must be noted that a simultaneous determination of diffusion properties of the rock mass such as the rock capacity factor and the distribution coefficient (using Eqn.7) is the advantage of through-diffusion experiments. In- or out-diffusion experiments will not produce these coefficients, making sorption experiments necessary to distinguish between the contribution of sorption and diffusion to the apparent diffusion coefficient.

Experimental Investigations

To develop a methodology for studying diffusion characteristics of the rock mass, a chalk sample from the Negev Desert, Israel, was used along
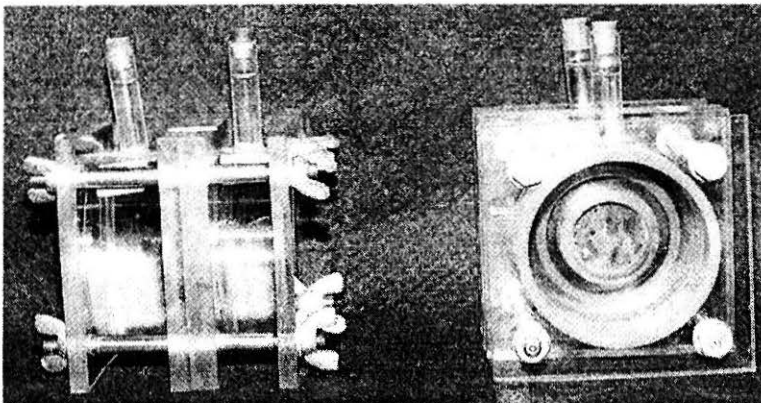

FIGURE 1 : Diffusion Cells Used in the Present Study

with strontium (Sr^{2+}) as the contaminant, in its chloride form. The experiments were conducted in the controlled constant temperature ($26 \pm 1.5°C$). Details of the test setup used are presented in the following.

As depicted in Fig.1, the diffusion cell, which is made of perspex, consists of two reservoirs, which are separated by a circular porous rock sample. The diffusive flux is observed between a reservoir cell with high concentration ($C_0 \approx 0.01$ M $SrCl_2 \cong 876$ ppm Sr^{2+}) across a porous rock sample of surface area, A, (= 26.42 cm²) and a receiving cell of volume, V, (= 300 cc) with zero initial concentration. After a transient phase, during which the solute partly accumulates in the rock matrix (dead-end pores and sorption), a constant flux between the cells and hence a linear breakthrough curve can be observed, as depicted in Fig.2.

A 10 mm thick rock sample was considered in the present study and to ensure its complete saturation, it was soaked in degassed millipore water and stored in a desiccator for two weeks. In order to avoid osmotically driven fluxes (Bradbury and Green, 1985) the receiving cell was filled with an isotonic solution. Any hydraulic gradient between the reservoir and receiving cell was avoided by replacing the sample volume (10 ml) in the receiving cell by the isotonic KCl solution. The concentration of strontium in the receiving cell was determined over a period of time using an Inductively Coupled Plasma (ICP) unit. Each time the sample was drawn out of the
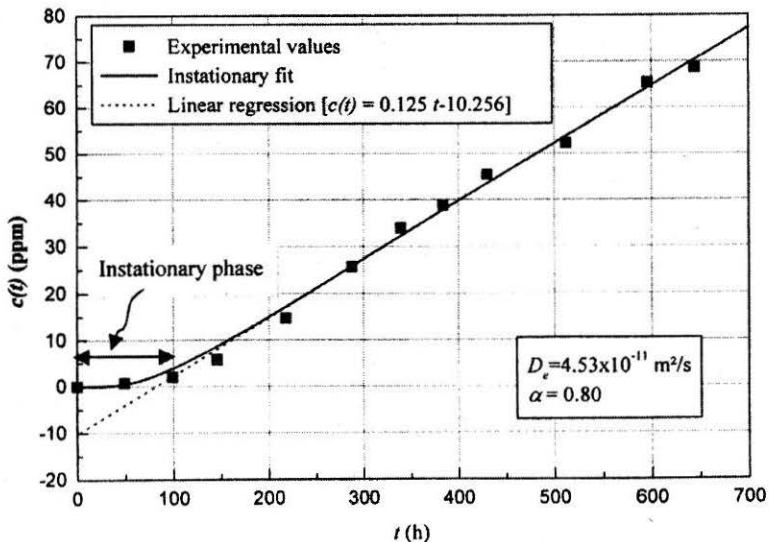

FIGURE 2 : Breakthrough Curve for Strontium Diffusing through a 10 mm Thick Chalk Sample

receiving cell, the computed concentration was corrected for dilution. At the completion of the experiment, porosity and the bulk density of sample were measured with the help of a Ultra Pycnometer (Quantachrome, USA). These are found to be equal to 33% and 1.651 g/cc, respectively.

An analytical solution for Fick's 2nd law for a porous slab, as proposed by Carslaw and Jaeger (1959) can be employed for defining the observed concentration change:

$$C(t) = \frac{AdC_0}{V} \left[\frac{D_e t}{d^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{\eta^2} \exp\left(-\frac{D_e \eta^2 \pi^2 t}{\alpha \, d^2} \right) \right] \qquad (10)$$

where C_0 denotes the concentration of the reservoir cell, d and A are the thickness and surface area of the rock sample, respectively. The two fit parameters, the effective diffusivity, D_e and the rock capacity factor, α, can be determined from Fig.2. The curve fitting procedure takes into account the transient phase of the breakthrough curve, i.e. the time to develop a linear concentration gradient in the rock sample, in determining of the diffusion coefficient and the rock capacity factor.

For the stationary phase of the experiment (t → ∞) the exponential term becomes zero and the following simplified relationship can be obtained (Bradbury and Green, 1985):

$$C(t) = \underbrace{\frac{AC_0 D_e}{Vd}}_{a} t - \alpha \underbrace{\frac{AdC_0}{6V}}_{b} \qquad (11)$$

hence,

$$D_e = a \frac{Vd}{AC_0} \qquad (12)$$

$$\alpha = b \frac{6V}{AdC_0} \qquad (13)$$

Results and Discussions

Figure 2 depicts a characteristic breakthrough curve observed for a chalk sample. Using the linear regression function of the stationary part of the breakthrough curve values of 'a' and 'b' are found to be 0.125 ppm/h and −10.256 ppm. Using Eqns.12 and 13, the effective diffusion coefficient, D_e, and the rock capacity factor, α, are found to be 4.53×10^{-11} m²/s and

0.803, respectively. Further, using Eqn.7, the distribution coefficient, K_d, is obtained as 0.29 cc/g. As expected, for the chalk sample with a small amount of clay minerals in it (Witthüser et al., 2003), the transport of strontium is only slightly retarded in the chalk matrix. The value of D_e is found to be in excellent agreement with the values reported in the literature being in the range of 9.19×10^{-12} to 8.72×10^{-11} m²/s (Witthüser et al., 2001). Hence an excellent reproducibility of diffusion coefficient determined by conducting the through-diffusion experiments can be observed. This demonstrates the efficiency of the methodology developed, and presented in this paper, for determining diffusion characteristics of the rock mass.

Concluding Remarks

As shown above through-diffusion experiments are a simple and reliable method to determine effective diffusion coefficients and rock capacity factors of the rock mass. However, several other diffusive transport phenomena in the porous media, which may occur, should be distinguished from the classical matrix diffusion (Moridis, 1999). In the case of a porous media with high sorption capacities like bituminous schist, it might be useful to describe surface-diffusion separately (Grathwohl, 1998), since it causes an additional transport in the direction of decreasing surface concentrations. Further, Moridis (1999) distinguishes diffusion in immobile, adhesive pore water (film-diffusion) and intraparticle-diffusion (diffusion into particles which constitute the porous matrix). However, it must be borne in mind that the diffusion characteristics obtained from the laboratory tests can be verified only by conducting field investigations.

Acknowledgements

References

BECKER, M.W. and SHAPIRO, A.M. (2000) : "Tracer Transport in Fractured Crystalline Rock: Evidence of Nondiffusive Breakthrough Tailing", *Water Resources Research*, Vol.36. No.7, pp.1677-1686.

BIRGERSSON, L. and NERETNIEKS, I. (1990) : "Diffusion in the Matrix of Granitic Rock: Field Test in the Stripa Mine", *Water Resources Research*, Vol.26, No.11, pp.2833-2842.

BRADBURY, M.H. and Green, A. (1985) : "Measurement of Important Parameters Determining Aqueous Phase Diffusion Rates through Crystalline Rock Matrices", *Journal of Hydrology*, Vol.82, pp.39-55.

CARMAN, P.C. (1956) : *Flow of Gases through Porous Media*, Academic Press Inc., New York.

CARSLAW, H.S. and JAGER, J.C. (1959) : *Conduction of Heat in Solids*, Clarendon Press, Oxford.

CRANK, J. (1975) : *The Mathematics of Diffusion*, Clarendon Press, Oxford.

FEENSTRA, S., CHERRY, J.A., SUDICKY, E.A. and HAQ, Z. (1984) : "Matrix Diffusion Effects on Contaminant Migration from an Injection Well in Fractured Sandstone", *Ground Water*, Vol.22, No.3, pp.307-316.

GRATHWOHL, P. (1998) : *Diffusion in Natural Porous Media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics*, Kluwer Academic, London.

HENRY, D.C. (1922) : "A Kinetic Theory of Adsorption", *Phil. Mag. Ser.*, Vol.6, No.44, pp.689-705.

KASS, W. (1998) : *Tracing Technique in Geohydrology*, A.A. Balkema, Lisse.

LEVER, D.A., and BRADBURY, M.H. (1985) : "Rock-Matrix Diffusion and Its Implications for Radionuclide Migration", *Mineralogical Magazine*, Vol.49, pp.245-254.

LEVER, D.A., BRADBURY, M.H. and HEMINGWAY, S.J. (1985) : "The Effect of Dead-End Porosity on Rock-Matrix Diffusion", *Journal of Hydrology*, Vol.80, pp.45-76.

MALOSZWESKI, P. (1994) : "Mathematical Modelling of Tracer Experiments in Fissured Rocks", *Freiburger Schriften zur Hydrologie 2*. Freiburg i. Breisgau.

MORIDIS, G.J. (1999) : "Semianalytical Solutions for Parameter Estimation in Diffusion cell Experiments", *Water Resources Research*, Vol.36, No.6, pp.1729-1740.

NERETNIEKS, I. (1980) : "Diffusion in the Rock Matrix: An Important Factor in Radionuclide Retardation", *Journal of Geophysical Research*, Vol.85, No.B8, pp.4379-4397.

SKAGIUS, K. and NERETNIEKS, I. (1988) : "Measurement of Cesium and Strontium Diffusion in Biotite Gneiss", *Water Resources Research*, Vol.24, No.1, pp.75-84.

TITS, J., JACOB, A., WIELAND, E. and SPIELER, P. (2003) : "Diffusion of Tritiated Water and $^{22}Na^+$ through Non-Degraded Hardened Cement Pastes", *Journal of Contaminant Hydrology*, Vol.61, pp.45-62.

WITTHÜSER, K., REICHERT, B. and HOTZL, H. (2001) : "Prognosis of Contaminant Transport Processes in Fractured Chalk: Laboratory Experiments and Numerical Studies", Seiler, K.P. and Wohnlich, S. (Ed.): New Approaches Characterizing Groundwater Flow Vol. 2, *Proc. of the XXXI Int. Association of Hydrogeologists Congress*, Munich, Germany, 10-14. September 2001. A.A. Balkema, Lisse, pp.1085-1089.

WITTHÜSER, K., REICHERT, B. and HOTZL, H. (2003) : "Contaminant Transport in Fractured Chalk: Laboratory and Field Experiments", *Ground Water*, 41(6): 806-815.

Notations

η	=	Accessible porosity
ρ	=	Bulk density
δ	=	Constrictivity factor
α	=	Rock capacity factor
τ	=	Tortuosity factor
η_e	=	Effective porosity
A	=	Surface area of the rock sample
a, b, n	=	Constants
c	=	Concentration
c(t)	=	Concentration at time 't'
C_0	=	Initial concentration of the solute
d	=	Thickness of the rock sample
D'	=	Relative diffusivity
D_a	=	Apparent diffusivity
D_m	=	Free water diffusivity
D_p	=	Pore diffusivity
J_d	=	Diffusive mass flux
K_d	=	distribution coefficient
L	=	Straight flow path length
L_e	=	Tortuos flow path length
t	=	Time
V	=	Volume of the receiving cell
X	=	Distance