Preferential flow phenomena in partially-saturated porous media

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Preface

The present report "Preferential flow phenomena in partially-saturated porous media" has been submitted as a part of the requirements for the Ph.D. degree at the Technical University of Denmark (DTU). The study has been taking place at the Institute of Hydrodynamics and Water Resources (now Environment and Resources (E&R)) in the period December 1997 to September 2001, with Professor Karsten Høgh Jensen as the primary advisor. The study was funded by the Danish Strategic Environmental Research Program (SMP).

The report is organized in three parts. Part 1 is a synopsis summarizing relevant literature including the work presented in this study. Part 2 and Part 3 are journal papers presenting the results from the two different subjects I have been working with during the Ph.D. period. The first paper "Visualization of microscale phase displacement processes in retention and outflow experiments: Nonuniqueness of unsaturated flow properties" is written in cooperation with Robert J. Glass, Karl Hollenbeck, and Karsten H. Jensen. The second paper "Multiple tracing experiments in unsaturated clayey till" is written in cooperation with Karsten H. Jensen, Bertel Nielsson, and René K. Juhler. The papers are not included in this www-version but can be obtained from the Library at Environment & Resources DTU, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Lyngby (library @er.dtu.dk).

The first paper is the result of a cooperation with Karl Hollenbeck, DTU and Robert J. Glass, Sandia National Laboratories, Albuquerque, New Mexico, USA. As a part of the Ph.D. requirements, I spent 3 months at Sandia National Laboratories working under the supervision of Robert J. Glass on non-uniqueness in unsaturated flow properties. The research idea was originally initiated by Karl Hollenbeck, and I acknowledge him for handing over the project to me. Working with Robert J. Glass was very inspiring and I learned many things about performing experiments, analyzing the results, and presenting them. I would like to thank him and the staff at the Flow Lab for making my stay there very pleasant.

The second paper presents the results of a field experiment in unsaturated clayey till. This study was performed in close cooperation with the Geological Survey of Denmark and Greenland (GEUS), and especially Bertel Nielsson from the Hydrology Department and René K. Juhler from the Geochemical Department. The fieldwork would not have been possible without the help of the two technicians Per Jensen from GEUS, and Klaus Fæster Hansen from E&R, DTU. They were always there to assist and help keeping up the spirit during the long field days (and nights).

I gratefully acknowledge Karsten for his competent guidance and unfailing support. Also thanks to the rest of my colleagues at the institute for creating a very nice atmosphere.

Lyngby, September 2001

Annette Pia Mortensen

Abstract

Preferential flow in unsaturated porous media, in the form of fingers and channels, has been observed to take place in different types of media and at different scales. The preferential flow is caused by fluid instabilities, created by density or viscosity differences, or because of heterogeneities in the geological media. In this study, two very different types of preferential flow problems are examined. In the first part, drainage processes in sand are visualized with the purpose of examining nonuniqueness found in experiments for measuring unsaturated hydraulic properties. In the second part, preferential flow in unsaturated fractured clayey till are examined by applying multiple tracing experiments.

Methods for measuring unsaturated hydrologic properties have shown to exhibit random and nonunique behavior. To examine the causes multiple retention and one-step outflow experiments were conducted on a thin sand sample. Light transmission techniques were applied during the experiments for visualizing the drainage processes at micro-scale. The drainage was found to be composed by a mixture of fast air fingering followed by a slower back-filling process. This fingering and back-filling was controlled by a combination of the size and the speed of the applied boundary step, small-scale heterogeneities, and the initial saturation and its structure. The mixture of these micro-scale processes had influence on the macroscale effective behavior and thereby also the measured unsaturated hydraulic properties. The results thus suggest limitations on the current definition and uniqueness of unsaturated hydraulic properties.

Fractures and macropores in clayey till may constitute fast preferential flow paths through an otherwise low-permeable porous media. To examine the influence of preferential flow in unsaturated clayey till, multiple tracing experiments were conducted in an isolated block at Avedøre, Denmark. Experiments were conducted at different steady-state water intensities, and multiple tracers with different molecular diffusion coefficients were applied to quantify the diffusive exchange between fractures and matrix. At high intensities, asymmetrical breakthrough curves were observed, where a fast peak was followed by a long tailing period. The multiple tracers only showed small differences in breakthrough indicating that diffusion processes only have small influence at high intensity and high water content. At the lowest intensity, a double peak behavior was observed for two of the applied tracers. This was hypothesized to be caused by severe retardation into the matrix. The tracer with the lowest molecular diffusion coefficient did not show the same double peak behavior, which may be caused by the differences in diffusion, however, sorption of the tracer may have influenced the transport as well. Colloids applied in the same experiment, peaked earlier than the solutes and did not show the double peak, which certifies that the colloids are experiencing less diffusion into stagnant water.

The double-porosity model CXTFIT was not fully capable of describing the observed breakthrough. The model fitted the data fairly well, however, unrealistically parameters were obtained and furthermore did different tracers result in different parameters. The simple mobile-immobile model thus partly failed to predict the transport, and different reasons were hypothesized including fingering and film flow in the fractures, heterogeneity in the matrix diffusion, and heterogeneity in the fractures.

Resumé

Præferentiel strømning i umættede porøse medier, i form af finger- og kanalstrømning, er blevet observeret i forskellige typer medier og på forskellig skala. De præferentielle strømninger opstår enten pga. instabilitet mellem de to væsker, fremkaldt af densitets- eller viskositetsforskelle, eller pga. heterogenitet. Præferentiel strømning i henholdsvis sand og ler er undersøgt i dette studie. I første del er dræningsprocesser i sand visualiseret med det formål at undersøge ikke-unikke resultater fundet ved bestemmelse af umættede hydrauliske parametre. Anden del af studiet beskriver tracer forsøg i sprækket moræneler udført med det formål at undersøge betydningen af præferentiel strømning på transport i umættede sprækker.

Forsøgsmetoder til bestemmelse af umættede hydrauliske parametre har tidligere vist både tilfældige og ikke-unikke resultater. Med henblik på at undersøge baggrunden for disse resultater blev retentions- og one-step forsøg udført på en tynd sandprøve. Ved at anvende lys transmission teknik under forsøgene kunne dræningsprocesserne visualiseres på mikroskala. Resulterne viste, at dræningen bestod dels af en hurtig luftfingerstrømning og dels af en efterfølgende mere langsom tilbagefyldningsproces. Både fingerstrømningen og tilbagefyldningen var kontrolleret af det påtrykte tryksteps størrelse og hastighed, af små-skala heterogenitet, samt den initielle mætning og dens fordeling. Kombinationen af disse mikroskala processer havde indflydelse på den effektive makroskala dræning og dermed også på bestemmelsen af de umættede hydrauliske parametre. Resultaterne antyder derfor en begrænsning i den unikke definition af umættede hydrauliske parametre.

Sprækker og makroporer i moræneler kan udgøre hurtige præferentielle flow kanaler i et traditionelt lav-permeabelt porøst medie. Med det formål at undersøge betydningen af præferentiel strømning i umættet moræneler, blev adskillige tracerforsøg udført i en isoleret blok ved Avedøre i Danmark. Forsøgene blev udført med forskellige konstante vandingsintensiteter, og ved at tilsætte flere tracere samtidigt, med forskellige molekylære diffusionskoefficienter, kunne den diffusive udveksling mellem sprækker og matrix vurderes. Ved høje vandingsintensiteter, blev traditionelle asymmetriske gennembrudskurver med et hurtigt peak og en efterfølgende lang hale observeret. Kun små forskelle i gennembrud blev fundet for de anvendte tracere, hvilket indikerer at diffusionsprocesserne kun har lidt inflydelse på transporten ved høj intensitet. Ved den laveste vandingsintensitet gav to af de anvendte tracere et dobbelt peak gennembrudsforløb, hvilket kan skyldes retardation pga diffusiv udveksling med matrix. Traceren med den laveste molekylære diffusionskoefficient gav ikke dette dobbelt peak, hvilket dels kan skyldes forskelle i diffusion og dels sorption. Kolloider tilsat som tracer i samme forsøg gav et tidligere gennembrudspeak end de opløste tracere og uden dobbelt peak, hvilket stemmer overens med at kolloider er udsat for mindre diffusion ind i stillestående vand end opløste tracere.

Den dobbelt-porøse model CXTFIT kunne ikke fuldt ud beskrive de observerede gennembrudskurver. Modellen fittede dataene rimeligt, men resulterede i delvist urealistiske parametre og derudover forskellige parametre for forskellige tracere. Den simple dobbelt-porøse model kan således kun delvist anvendes til at beregne sprækketransporten, hvilket tildels begrundes med fingerstrømning og film flow i sprækkerne, heterogenitet i matrix diffusion samt heterogenitet i sprækkerne.

Contents

PART 1

Preferential flow phenomena in partially-saturated porous media

1 Preferential flow phenomena in partially-saturated porous media

1.1 Introduction

Unsaturated hydrology has achieved increased attention within the last decades. The field describes the processes taken place in the unsaturated zone, or the so-called vadose zone, found between the ground surface and the groundwater table. The most important processes in the unsaturated zone include evaporation, plant-soil interactions, water infiltration, and contaminant transport. These processes control, e.g., the formation of groundwater, the transport of chemicals, and various remediation technologies. Different types of geological media are found in the unsaturated zone, ranging from relatively homogenous sand to heterogeneous fractured media. Within these different types of media preferential flow and transport have been observed. Preferential flow in the vadose zone is the focusing of flow into narrow channels or fingers. This may occur as a result of fluid instabilities, created by density or viscosity differences, or because of heterogeneities in the geological media like material interfaces and structures. In this study two very different types of preferential flow in unsaturated porous media are examined. The first part describes micro-scale processes within drainage experiments in homogenous sand conducted to determine unsaturated hydraulic properties. The second part describes flow and transport in unsaturated clayey till where fractures constitute fast preferential flow paths.

Determining unsaturated hydraulic properties in the form of retention characteristics and unsaturated hydraulic conductivity characteristics is necessary to describe and model unsaturated flow and transport. Traditionally these properties are determined by steady-state retention curve experiments or transient one-step and multistep outflow experiments. Recently, it has been documented that the methods may show random and nonunique behavior. The problems include lack of reproducibility both when performing experiments on several but essentially identical samples of the same media and when repeating experiments on the same sample. Also discrepancies are found in between experiments performed at different flow rates, at different scales, and also when using different methods. Many possible reasons for these problems have been suggested including initial saturation, sample heterogeneity, phase fragmentation, and air and water entrapment. The purpose of the current study was to quantify the reasons for this random and nonunique behavior by applying visualization techniques and thereby reveal the underlying micro-scale processes.

Fractures and macropores, which are found in stiff soils like clay, may constitute preferential flow paths through an otherwise low-permeable medium. These microscopic structures affect water and solute transport at the macroscopic level by creating nonuniform flow fields where the velocity may be several orders of magnitude larger than in the surrounding matrix. These preferential flow-paths thus constitute a risk for chemicals, e.g., pesticides, to be transported at high velocities over long distances. Non-equilibrium transport processes may develop in fractured media, where diffusive exchange between fractures and matrix retard the transport of chemicals. Understanding this transport is important for the prediction of for example pesticides leaching to the groundwater. Previous experiments in clayey till have mainly been taken place at saturated conditions, whereas the knowledge of fracture flow and transport in the vadose zone is rather limited. A serious limitation in fracture experiments is the problem of obtaining representative monitoring and sampling. Previous experiments have included small-scale laboratory experiments in soil-

monoliths, intermediate-scale lysimeter and dye-tracer experiments, and large-scale tile-drain experiments. The purpose of the current study was to conduct highly controlled tracer experiments in unsaturated fractured clayey till. To circumvent the sampling problem the experiments took place in an isolated block where flux-averaged breakthrough curves could be monitored. To evaluate the influence of diffusive exchange on the transport, multiple tracing techniques were applied.

The report is organized in three parts:

Part 1: "Preferential flow phenomena in partially-saturated porous media" is a synopsis, which introduces the two subjects of the Ph.D. study. Recent literature including the results from the current study is summarized. The synopsis is roughly divided into two parts, where Section 1.2-1.5 focus on unsaturated hydraulic properties and Section 1.6-1.8 describes fracture flow and transport.

Part 2: "Visualization of microscale phase displacement processes in retention and outflow experiments: Nonuniqueness of unsaturated flow properties" is a journal paper presenting the results from the study on unsaturated hydraulic properties.

Part 3: "Multiple tracing experiments in unsaturated clayey till" is a journal paper manuscript presenting the results from the study on flow and transport in partially saturated fractured clayey till.

1.2 Unsaturated flow in porous media

The most common two-phase problem in porous media is the flow of air and water. This is for example found in the unsaturated zone, or the so-called vadose zone, where water infiltrates through partly saturated pores to the groundwater. Liquid flow in the unsaturated zone is controlled by a combination of gravitational, capillary, and viscous forces. At the macroscopic scale, the flow in unsaturated porous media is usually described by the highly nonlinear Richards' equation given by:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\psi)\left(\frac{\partial \psi}{\partial z} + 1 \right) \right] \tag{1.1}$$

where θ is the volumetric water content, ψ is the soil water pressure [m], K is the hydraulic conductivity [m/s], z is the distance [m], and t is the time [s]. The equation assumes that flow is laminar, that the effect of displaced air during infiltration can be neglected, and that air pressure, temperature, liquid density and viscosity are constant.

The equation contains two functional relationships characterizing the soil: (1) the unsaturated hydraulic conductivity function, $K(\theta)$, describing the relation between unsaturated hydraulic conductivity and water content, and (2) the soil-water retention function, $\psi(\theta)$, describing the relation between pressure and water content. To solve Richards equation, prior knowledge of these unsaturated hydraulic properties are required. Methods for determining the unsaturated hydraulic properties are described in Section 1.3.1

1.2.1 Preferential flow and fingering

Two different types of immiscible flow are found in porous media: (1) transient displacement classified as either drainage or imbibition, and (2) steady state flow [*Dullien, 1992*]. During transient displacement complex patterns can be found where preferential flow paths in the form of fingers develop. The fingering phenomenon is shortly described below, with focus on the fingers developing in drainage experiments.

The relative magnitude of the forces involved in transient displacement can be quantified by three dimensionless parameters: the capillary number, Ca, the bond number, B, and the viscosity ratio, M. The capillary number describes the relative magnitude of viscosity over capillary forces, the bond number describes the relative magnitude of gravity over capillary forces, and the viscosity ratio gives the ratio of the two viscosities [*Wilkinson, 1984; Lenormand, 1990*]:

$$Ca = \frac{\text{viscous forces}}{\text{capillary forces}} = \frac{v\mu_2}{\gamma \cos\varphi} \tag{1.2}$$

$$B = \frac{\text{gravity forces}}{\text{capillary forces}} = \frac{\Delta\rho g R^2}{\gamma \cos\varphi} \tag{1.3}$$

$$M = \frac{\mu_2}{\mu_1} \tag{1.4}$$

where index 1 and 2 represents the displaced fluid and the displacing fluid, respectively, v is the velocity [m/s], μ is the viscosity [kg/ms], γ is the interfacial tension [N/m], φ is the contact angle

between the fluid and the solid surface, $\Delta\rho$ is the density difference between the two fluids [kg/m^3], R is the grain size [m], and g is the gravitational acceleration constant [m/s^2].

Preferential flow or fingering can arise as a result of fluid instabilities created by density or viscosity differences between the two immiscible fluids or because of heterogeneities in the geological media [*Kueper and Frind, 1988*]. The stability of an invading front is controlled by the interplay between viscous and gravitational forces that can act as either stabilizing or destabilizing [*Glass and Nicholl, 1996*]. Viscous instability occurs when a less viscous fluid displaces a more viscous fluid and gravitational forces do not act to fully stabilize the interface, which for example may occur when extraction oil. Gravitational instability occurs when a denser fluid displaces a lighter one from above, and viscous forces do not act to fully stabilize the front. The gravity fingering may thus for example take place when water infiltrates into unsaturated porous media.

A first order linear stability analysis can be performed to examine the onset of instability in homogenous media. The fingering criteria are functions of the surface tension, interfacial velocity in the direction of the flow, and the density and viscosity differences between the two fluids. In natural media, complicating factors like uniform and nonuniform initial saturation, wetability of the soil, media heterogeneities and the existence of large void spaces such as macropores and fractures can have fundamentally effect on the fingering process. These factors are not described by the linear stability analysis, which limits its use in natural soils [*Glass and Nicholl, 1996*].

In drainage, three main regimes for the displacement of a wetting fluid by a nonwetting fluid exist: (1) capillary fingering, (2) viscous fingering, and (3) stable displacement [*Lenormand et al., 1988*]. Capillary fingering is found at low capillary number, where viscous forces in both fluids are negligible. This type of fingers can grow in all directions, even backward, and may form loops that entrap the displaced fluid. At low flow-rate the finger advancement are observed to take place in a Haines jump pore-filling mechanism [*Glass and Yarrington, 1996*]. Localized Haines jumps occur as the meniscus in an individual pore becomes unstable and moves rapidly to fill or empty the pore at a rate, which is not determined by the flow rate, but rather local capillary, viscous and inertial forces [*Wilkinson, 1984*]. Viscous fingering form at high flow rates when viscous forces are dominant, and capillary effects and pressure drop in the displacing fluid are negligible (large M values) [*Lenormand et al., 1988*]. They form tree-like fingers, without loops, that grow in the direction of the flow. Stable displacement takes place if viscosity forces are dominant, and capillary effects and pressure drop in the displaced fluid are negligible (small M values). Here a flat front develops with only a few irregularities of a few pores [*Lenormand et al., 1988; Lenormand, 1990*]. The three regimes can be represented by the following statistical models: (1) invasion percolation for capillary fingering, (2) diffusion limited aggregation for viscous fingering, and (3) anti diffusion limited aggregation for stable displacement [*Lenormand, 1990*].

1.3 Unsaturated hydraulic properties

Description of flow and transport in the unsaturated zone by Richards equation requires knowledge of the unsaturated hydraulic properties, i.e., the unsaturated hydraulic conductivity curve, $K(\theta)$, and the retention curve, $\theta(\psi)$. The functional relationships have been parameterized by several researchers, where the most common applied model is by *van Genuchten* [1980]. The retention characteristics are represented by:

$$S_e = \left[1 + (\alpha\psi)^n\right]^{-m} \tag{1.5}$$

where S_e is the effective saturation, $S_e=(\theta-\theta_r)/(\theta_s-\theta_r)$, θ is the water content, θ_s and θ_r is the water content at full and residual saturation, respectively, and α, n, and m are empirical parameters, m=1-1/n. The unsaturated hydraulic conductivity is represented by:

$$K = K_s S_e^{1/2}\left[1 - \left(- S_e^{1/m}\right)^m\right]^2 \tag{1.6}$$

where K is the unsaturated hydraulic conductivity [m/s] and K_s is the saturated hydraulic conductivity [m/s].

1.3.1 Measurement of unsaturated hydraulic properties

Various field and laboratory methods for determining unsaturated hydraulic properties have been proposed. The laboratory methods have developed from traditional static equilibrium and steady state methods [e.g., *Klute, 1986; Corey, 1985*] to dynamic experiments where nonlinear inversion procedures are employed [see review by *Hopmans and Simunek, 1999*]. The standard experimental set-up used for measuring unsaturated hydraulic properties consists of a small laboratory column where the saturated porous sample is placed on a porous plate that only allows water to exit. Drainage of the sample is initiated by imposing one or several differential phase pressures on the system, either by increasing the air pressure relative to the water or by decreasing the water pressure relative to the air.

In the traditional static equilibrium method for measuring the retention curve a series of small step changes in capillary pressure are imposed. For each pressure step equilibrium is awaited and the amount of water leaving the system is measured and converted into sample average water content, resulting in a direct determination of the equilibrium retention curve. The major drawback of the method is that it is time-consuming and elaborate, since equilibrium for each pressure step has to be awaited. *Wildenschild et al.* [1997] used a syringe pump technique, where water continuously was withdrawn from the soil sample at very low rate, to measure the retention curve directly. This method is faster and provides accurate measurements that compare with the static retention curves.

An alternative method, that provide fast determination of both the retention curve and the unsaturated hydraulic conductivity function is the transient one-step and multistep outflow experiments. By imposing one or several pressure steps to the cell and measuring the outflow as a function of time, inverse estimation can be employed to determine the unsaturated hydraulic properties. In the optimization procedure, Richards' equation is solved numerically using the parameterized hydraulic functions with initial estimates for their parameters. These parameters are optimized by minimizing an objective function containing the sums of squared deviations between observed and predicted flow variables, using repeated numerical simulation of the flow process. The one-step outflow experiment, where only one pressure step is imposed, was the first method introduced [*Kool et al., 1985*]. Problems with nonuniqueness in the optimization procedure were however encountered, where several sets of parameters gave minimum values of the objective function. Reliable estimation could only be obtained if independently measured retention data were included in the one-step outflow optimization procedure [e.g., *van Dam, 1992*]. To circumvent the need for additional retention data in the outflow method, the multistep outflow experiment was introduced. By applying the pressure in several small steps and measuring the outflow as a function

of time, unique parameter values were obtained [*van Dam et al., 1994; Eching et al., 1994*]. The parameter estimation technique has also been applied successfully to other laboratory techniques, like the evaporation experiments, but the methods will not be described here [see review by *Hopmans and Simunek, 1999*].

1.3.2 Non-uniqueness of unsaturated hydraulic properties

Several problems have been encountered with the methods for determining unsaturated hydraulic properties. These include lack of reproducibility, both when repeating the same experiment on the same sample [*Hollenbeck and Jensen, 1998*] or on several but essentially identical samples of the same porous media [*van Dam et al., 1994*]. Also discrepancies have been found between experiments performed at different flow rates [*Wildenschild et al., 2001*], experiments using different methods [*Stolte et al., 1994*] and experiments at different scales [*Kasteel et al., 1999*].

Hopmans et al. [1992] applied X-ray computed tomography to visualize the drainage processes during one-step experiments. They found that drainage takes place from the top downward until air continuity is established. This does not conform to Richards type of flow, which assumes that the air phase is continuous throughout the soil sample. By repeating the experiments with an initially unsaturated sample they found that drainage now occurred in the whole sample. They concluded that unfavorable conditions in the drainage processes exit if the soil is initially saturated and suggested that better results are obtained if the sample is initially unsaturated as the pressure is imposed, because of continuation in the air phase. However, the images also revealed nonuniform drainage, with preferential flowpaths along the cell walls and air blockage at the porous plate interface along with patches and bands of wet and dry regions within the drained sample. The resolution of the images, however, limited detailed study of the drainage processes.

Wildenschild et al. [2001] performed a series of both quasi-static retention experiments, using the syringe pump method as described above, and one-step and multistep outflow experiments on a sandy and a loamy soil to evaluate the influence of flow rate on the unsaturated hydraulic properties. For the sandy soil differences in the drainage were found for the three methods. In general, soil water retention and thereby residual water content increased as the number of steps decreased. The largest retention and residual water content was found for the one-step experiment and the lowest retention and residual water content for the quasi-static syringe pump and the low-pressure multistep outflow experiments. Water entrapment and pore blockage was hypothesized as the main reasons for the observed phenomena at high flow rates, as well as lack of air continuity in the sample during the wettest stages of the experiment. The loamy soil did not show the same dependence on the flow rate, maybe because of the wider pore-size distribution of the loamy soil compared to the sand.

Hollenbeck and Jensen [1998] performed a series of single and multistep outflow experiments on the same sand-sample and found both random and nonunique behavior. One-step outflow experiments applying small pressure steps resulted in different outflow responses using the same boundary step. One-step outflow experiments with high pressure steps had good repeatability, however, the same outflow responses were obtained at different boundary steps. The results thus suggested serious limitation of inverse methods for hydraulic parameter estimation from transient outflow experiments. The reason for this random and non-unique behavior could only be speculated upon. The main cause of the identical outflow responses for different experiments was

hypothesized to be phase fragmentation during rapid flow, causing entrapment of the water phase. Additional, random microscale heterogeneity characteristics and/or the initial distribution of phases were suggested to might have predominantly determined the outflow response.

To reveal the causes for the random and nonunique behavior observed by *Hollenbeck and Jensen* [1998] visualization of the drainage processes during equilibrium retention curve experiments and multiple one-step outflow experiments were conducted by *Mortensen et al.* [2001a]. The experiments were performed on a thin 10 cm x 10 cm x 1 mm cell, filled with the same sand type as examined by *Hollenbeck and Jensen* [1998]. All experiments were performed on the same sand-pack to maintain the same small-scale heterogeneity in each experiment. Micro-scale drainage processes were recorded by applying the light transmission technique of *Tidwell and Glass* [1994]. The 1 mm thin and thus translucent sand sample was placed in front of a constant light source and images were recorded with a CDD (charge-coupled-device) camera. Because of the difference between the refractive indices of the sand-air and sand-water interfaces, the transmitted light is reduced when air replaces water allowing the drainage processes to be followed in details. Also traditional macro-scale response in the form of cumulative outflow as a function of time was measured to reveal the influence of micro-scale processes on the macro-scale response. All experimental details, including saturation procedure (to assure 100% initial saturation), settling of sand (to avoid changes in the sand-pack during the experimental period), pressure steps (to assure the same pressure step in replicate experiments), and temperature (to avoid viscosity changes) were controlled to assure repeatability. Additionally, the images were gray level adjusted and corrected for shifting to assure that all images from the experimental period could be compared at micro scale.

The images revealed that the drainage process was composed of two steps. First, fast capillary fingering was observed immediately after a change in pressure was imposed to the cell. Second, a slower back-filling process behind the front was observed to take place. Thus water behind the front was not entrapped but could continue to drain. The viscous differences between the air and water, however, resulted in very different time scales for the fast fingering and the subsequent back-filling. Additional advance of the front during the back-filling process was observed in the form of local Haines jumps. At small pressure steps the equilibrium images thus showed a near-horizontal gravity stabilized drainage front that was influenced by small-scale heterogeneities, both at the front where the heterogeneities influenced the growth of fingers and behind the front where small pores were left saturated. At high pressure steps, air was observed to finger down to the porous plate, and because of the locally larger pores near the plate the air moved horizontally. A desaturated zone above the porous plate was thereby created, which drastically reduced the flow of water and basically stopped further drainage of the cell.

The different drainage processes were observed in all experiments, but based on the experimental method and the size of the applied pressure step, differences in the results were observed. The one-step experiments were performed at five different pressure steps each with three replicates. The reproducibility was high for all experiments and the random behavior observed by *Hollenbeck and Jensen* [1998] at small pressure steps was not observed. At high pressure steps, the same outflow response was measured for different pressure steps, which was in agreement with the results of *Hollenbeck and Jensen* [1998]. The reason for this nonuniqueness was found to be air blocking the porous plate, and thereby isolating the sand from further drainage. This closure occurred at all high

pressure steps, thus resulting in the same outflow response regarding the difference in pressure step. Additional one-step experiments were performed to examine the influence of initial saturation on the drainage process. Two different realizations of incomplete initial saturation structures were created. They both had a mean initial saturation of 0.91, however, the structure of the entrapped air was very different in the two experiments. The obtained outflow response for the two experiments showed large differences, also compared to the corresponding initially fully saturated experiment, implying that the initial saturation and especially its structure have influence on the fingering and the drainage processes. This is likely what caused the random behavior observed by *Hollenbeck and Jensen* [1998] at small pressure steps. Their saturation procedure resulted in mean initial saturation values of 0.886 and likely with different structures for each experiment.

Comparing the final images from the one-step outflow experiments with the final images from the equilibrium retention curve experiment at the corresponding pressure step, differences in drainage as a function of the speed of the applied pressure step was examined. At small pressure steps only small differences between the drainage for one-step and equilibrium retention experiments were observed. At high pressure steps, the air blocking the porous plate resulted in very different drainage process for the one-step and the equilibrium retention experiment. In the latter, the back-filling process as described above has been allowed to take place for each intermediate pressure step, resulting in a fairly homogenous drainage front in the cell. In the one-step experiment, the air closes the porous plate and prevents the back-filling to take place, thereby resulting in a highly heterogeneous drainage. Because of the differences in back-filling, more water has drained in the equilibrium retention experiment, resulting in a mean residual saturation of 0.41 cm, compared to the one-step experiment where the mean residual saturation was 0.57. These results compare to the findings of *Wildenschild et al*. [2001] where the highest residual saturation was found for the one-step experiment.

In conclusion, the drainage process was found to be composed of fast air fingering followed by a slower back-filling. The drainage was influenced by the size and the speed of the pressure step, by small-scale heterogeneities, and by the initial saturation and its structure. Micro-scale processes thus control the macro-scale outflow response traditionally measured, which suggest limitations in the current methods for determining unsaturated hydraulic properties.

1.4 Preferential flow in fractured porous media

Preferential flow in natural media is often caused by different scales of heterogeneity. Large connected void spaces, such as fractures, fissures, cracks, and macropores, may constitute preferential flow paths within a low-permeable porous medium. Fractures, defined as planar stress features, can be found in many stiff soils, e.g., clay deposits, and in most near surface rock units. In rock units, tectonic movements are the main cause of fractures, whereas several processes including desiccation and freeze/thaw processes, and ice-tectonic movements create fractures in clay deposits [*Klint and Gravesen, 1999*]. Macropores are found in many types of soils and are typically of organic origin, including worm holes, animal burrows, and root channels.

Clayey tills cover large parts of northern Europe and America, where they typical overlay sand, gravel, bedrock, or limestone aquifers. Because of the low permeability of the thick clay deposits, they have previously been expected to protect the underlying groundwater aquifers. However, macroscale heterogeneities like fractures and macropores have recently been recognized to create preferential flow paths within the low-permeable clayey till. The flow velocities within these preferential flow paths can be orders of magnitude higher than in the surrounding clay matrix, and they thereby constitute a risk for transport of contaminants to the underlying aquifers. Chemicals, like e.g. pesticides that under normal circumstances would sorb to clay materials, may thereby be transported over long distances at a high velocity. Fractures and macropores in clayey till together with unweathered/weathered transitions, layering, and sandlenses create a very heterogeneous flow system that complicates the description and prediction of flow and transport. Seasonal variations in the groundwater table will add to this complexity since the upper part of the clay deposit will change between saturated and unsaturated conditions.

The following sections describe flow and transport processes in both saturated and unsaturated fractured systems. In Section 1.7 different tracing techniques in fractured media are presented and in Section 1.8 modeling approaches relevant for fractured media are described.

1.5 Fluid flow in fractured porous media

1.5.1 Fluid flow in saturated fractured porous media

Fundamentally, flow through a single fracture is governed by the Navier-Stokes equations. The only fracture geometry where the Navier-Stokes equations can be solved exactly is a fracture bounded by smooth, parallel walls [*Zimmerman and Yeo, 2000*]. Assuming laminar flow in a parallel plate fracture separated by a distance b the hydraulic conductivity is given by [*Witherspoon et al. 1980*]:

$$K_f = \frac{\rho g}{12\mu} b^2 \tag{1.7}$$

where K_f is the hydraulic conductivity of the fracture [m/s], ρ is the fluid density [kg/m^3], g is the acceleration of gravity [m/s^2], μ is the fluid viscosity [kg/ms], and b is the aperture [m]. The flow rate through the fracture can be determined from Darcy's law [*Witherspoon et al. 1980*]:

$$Q = \frac{\rho g}{12\mu} b^3 \frac{\Delta h}{L} W \tag{1.8}$$

where Q is the flow rate [m^3/s], h is the hydraulic head [m], L is the flow path length [m], and W is the fracture breadth [m]. Equation (1.8) is known as the cubic law because of the proportionality between the flow rate and the third power of the aperture.

The cubic law has been validated experimentally in open smooth-walled fractures [*Witherspoon et al., 1980*], but several studies have shown that the parallel plate model is inadequate to describe flow in natural fractures. The deviation arises from the large variability in aperture in heterogeneous rough walled fractures where the walls can contact each other at discrete points. Applying the cubic law for estimation of a mean aperture in a natural fracture will thus underestimate the aperture because the local heterogeneities will control the pressure drop [*Zimmerman and Yeo, 2000; Tsang, 1992*]. Another drawback of the parallel plate model is that heterogeneity in natural fractures result in the development of preferential flow paths the so-called channels [*Moreno and Tsang, 1991; Birkholzer and Tsang, 1997; Brown et al., 1998*]. The channels develop along interconnected zones of high permeabilities where the least resistivity to flow is found. The channeling will lead to numerous small dead-end zones in the fracture plane with stagnant water that do not take part in the macroscopic flow. A complete description of this complex flow pattern in a natural flow system is not possible. However, the recognition of flow channeling in fractures is important for understanding chemical transport in fractured media (see Section 1.6) and when modeling fracture flow and transport (see Section 1.8)

Flow in fractured media can be divided into three different categories: (1) flow in a nonporous fractured system where flow and transport in the matrix is negligible; (2) flow in a porous fractured system where flow in the matrix is neglected but a diffusive exchange between the fracture and matrix are allowed; and (3) flow in a permeable fractured system where flow and transport are allowed in both fractures and matrix. The double porous approach with a mobile (fracture) and immobile (matrix) flow system is most common under saturated conditions. This is because the saturated hydraulic conductivity of the matrix generally is several orders of magnitude smaller than the saturated conductivity of the fractures, allowing fluid flow in the matrix to be considered negligible.

A natural fracture network in the field is traditionally described by fracture parameters like spacing, strike and aperture. However, the flow in a fracture network will also depend strongly on the connectivity of the fractures, but because of the difficulties in determining the connectivity of fractures in the field, this geometric feature is traditionally not included in network descriptions [*National Research Council Committee on Fracture Characterization and Fluid Flow, 1996; Pruess, 2000*].

1.5.2 Flow in unsaturated fractured porous media

In unsaturated fractured porous media, where both water and air are present, the flow pattern becomes highly complex. The flow in unsaturated fractures depends both on the media structure and on the three main forces: capillary, viscous, and gravitational. This implies that factors like initial saturation and its distribution, matrix wettablity, and entrapment of air have influence on the flow structure. The effect of capillary, viscous and gravitational forces are relatively well understood in porous media (see Section 1.2), but their coupling effects in fractured media are not well understood and cause uncertainty in predictions of flow and transport [*Faybishenko et al., 2000*].

Early conceptual models for unsaturated flow in fractured media assumed that fractures were either fully water saturated or fully desaturated [*Wang and Narasimhan, 1985; Pruess and Tsang, 1990*]. This assumption was based on capillary theory that predicts that the critical aperture, d^*, determining the saturation of a fracture is given by the Young-LaPlace equation $d^*=2\gamma/P_c$ where γ is the surface tension [N/m] and P_c the capillary pressure [Pa]. Fractures having aperture $d < d^*$ are filled with water, whereas regions having aperture $d > d^*$ are filled with air [*Pruess and Tsang, 1990*]. This implies that large fractures will be dry and act as capillary barriers, and only the matrix or small fractures are able to conduct water. Before the fractures can contain water, the capillary theory also predicts that the matrix must be saturated. Thus water entering an unsaturated fractured porous medium will fill up the smallest pores first, and not before the matrix is saturated will macropores and fractures start to conduct water.

Recently, preferential flow paths in the form of film flow and fingering have been observed in unsaturated fractures. Film flow along fracture planes that are not perfectly horizontal has been observed by *Tokunaga and Wan* [1997]. The film fills in the regions of small-scale roughness and its thickness depends on the capillary pressure. For a fast film to develop, near-zero matrix potentials (i.e. near saturated matrix) are required [*Tokunaga et al., 2000*]. Preferential flow in the form of fingering has also been observed in unsaturated fractures, even when the matrix is unsaturated [*Glass and Nicholl, 1996*]. Flow in unsaturated fractures in the presence of an unsaturated matrix can take place if the applied water flux is larger than the infiltration capacity of the matrix, resulting in ponded infiltration, or where local heterogeneity provides a direct support of water [*Glass and Nicholl, 1996*]. *Su et al.* [2000] conclude that flow in unsaturated fractures is more likely to proceed as localized fingers due to gravitational instabilities or variability in fracture size rather than as a smooth sheet that fills the entire plane of the fracture. Gravity driven fingers may develop in nonhorizontal fractures because of the gravitational instability occurring when a denser fluid displaces a lighter one from above and viscous forces do not act to fully stabilize the front [*Nicholl et al., 1994*]. Thus, gravity driven fingers in unsaturated fractures is a different phenomenon that the heterogeneity induced channeling found in saturated natural fractures.

Several researchers have found that the finger geometry changes rapidly over time and result in an intermittent flow structure. *Su et al.* [1999] conducted a series of visualization experiments that demonstrated that infiltrating water proceeds through unsaturated fractures along nonuniform, localized preferential flow paths. Even though constant inlet conditions were maintained, pervasive unsteady and intermittent flow was observed, where portions of the flow channel underwent cycles of snapping and reforming. The intermittent flow was hypothesized to be caused by liquid flowing through a sequence of small to large to small apertures. *Persoff and Pruess* [1995] also observed unsteady flow in unsaturated fractures in the form of persistent instabilities with cyclic pressure and flow rate variations even under constant applied boundary conditions. They concluded that the redistribution of entrapped air created spatial and temporal flow instabilities. *Dahan et al.* [2000] examined fluid flow through vadose zone chalk. They found that the flow take place in a few dissolution channels where fluxes and flow trajectories vary in both time and space. These observations of nonsteady flow structures under steady state conditions suggest that chaos theory is applicable to certain aspects of fluid flow and mass transport through unsaturated fractures [*Glass and Nicholl, 1996; Pruess et al., 1999*].

The experimental investigations suggest that conventional volume-average approaches for calculating transport of contaminants in unsaturated fractured media are not applicable to describe flow in unsaturated fractures, since preferential flow like fingering and film flow is not predicted by these models. Thus, conventional models will underpredict the fast transport of contaminants that the preferential flow along fractures will cause. Invasion percolation theory has been applied to small-scale experiments in the laboratory to describe the fingering observed in unsaturated fractured media. However, it is not obvious how invasion percolation can be applied for specific flow and transport behavior at actual field sites [*Pruess et al., 1999*]. The different modeling approaches applied to fractured media are described in Section 1.8.

1.6 Transport in fractured media

Transport in fractured media is complicated by the preferential flow patterns found in both saturated and unsaturated fractures. Transport studies have shown that breakthrough curves obtained in fractured media are generally asymmetrical, where the effluent solute concentration peaks early followed by a long tailing period with low concentrations. The most common explanation for this asymmetrical behavior is diffusive exchange between fractures and matrix, resulting in nonequilibrium transport processes [*Brusseau, 1993; Hu and Brusseau, 1995*]. In a mobile-immobile system, advective and dispersive transport will take place in the mobile domains, i.e., in the fractures. Flow in the surrounding matrix is normally several orders of magnitude smaller and can thereby be considered immobile, which reduces the transport processes to molecular diffusion. Between the two domains large concentration gradients will cause a diffusive gradient towards the matrix. Depending on the porosity of the matrix, the velocity in the fractures, and the molecular diffusion coefficient of the solute, diffusive exchange between the fractures and the matrix, the so-called matrix diffusion, may take place. Other processes in fractured media may cause asymmetrical breakthrough curves as well. The strong heterogeneity of a fractured media may cause non-Fickian dispersion and additionally will kinetic sorption result in the same breakthrough behavior, where a peak is followed by a long tailing period.

The following description of transport in fractured media will focus on conservative solutes, i.e. retardation processes like sorption and degradation are not included. Afterwards transport of colloids is shortly presented.

1.6.1 Solute transport in fractured porous media

Different methods of describing transport in fractured media exist, depending of the applied mass balance. A common method is to consider the solute mass balance for the mobile zone and account for diffusive exchange between fractures and matrix by including a sink/source term in the convection-dispersion equation. The general 1-D transport equation for steady-state flow with a conservative tracer in a mobile-immobile system is thus given by [*van Genuchten and Wierenga, 1976; van Genuchten and Wagenet, 1989*]:

$$\theta_m \frac{\partial c_m}{\partial t} + \theta_{im} \frac{\partial c_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - \theta_m v_m \frac{\partial c_m}{\partial x} \tag{1.9}$$

where index m and im represent the mobile and immobile zones, respectively, c is the concentration [kg/m^3], t is the time [s], θ is the water content, D is the hydrodynamic dispersion coefficient [m^2/s], and v is the mean flux [m/s].

The dispersion in fractures and the diffusive exchange between fractures and matrix will be discussed below, and limitations in the current description are discussed.

Dispersion in fractured media

The dispersive flux of solutes in a homogeneous medium is an extension of the Fick's law of diffusion:

$$J = -D\nabla c \tag{1.10}$$

where D is the dispersion tensor, traditionally divided into an advective and a diffusive component:

$$D = D_{mec} + D_e \tag{1.11}$$

where D_{mec} is the mechanical dispersion [m^2/s] and D_e is the effective diffusion coefficient [m^2/s]. The mechanical dispersion accounts for the spreading taking place in the media. In a porous media the mechanical dispersion accounts for: (1) microscale spreading because of the parabolic velocity distribution in single pores, (2) variability in velocities between different pores, and (3) the tortuous flow path between the grains. For a homogenous porous media, the mechanical dispersion is usually expressed as a linear function of the pore water velocity:

$$D_{mec} = \alpha v \tag{1.12}$$

where α is the dispersivity of the porous media [m]. For unsaturated conditions the dispersivity will depend on the water content. The effective diffusion is a function of the molecular diffusion coefficient of the solute in water and the tortuosity of the media or the fracture; where the tortuosity reflects the reduced rate of molecular diffusion in a geometrically complex void space:

$$D_e = \tau D_0 \tag{1.13}$$

where D_0 is the free water diffusion coefficient [m^2/s] and τ is the tortuosity (< 1).

In a variable aperture fracture, the dispersion of solutes also results from a combination of molecular diffusion and mechanical dispersion. The mechanical dispersion is caused by two different mechanisms: (1) the Taylor dispersion, which results from velocity variations across the fracture aperture, and (2) the macrodispersion (also known as the geometric dispersion), which is caused by velocity variations in the planar of the fracture because of aperture variability [*Roux et al., 1998; Detwiler et al., 2000*]. The importance of the different mechanisms is traditionally analyzed in terms of the nondimensional Peclet number [*de Marsily, 1984*]:

$$Pe = \frac{v\,b}{D_0} \tag{1.14}$$

where Pe is the Peclet number, and b is a characteristic length (e.g., fracture aperture) [m].

In a parallel-plate fracture the primary mechanism causing dispersion is the parabolic velocity distribution across the fracture. This Taylor dispersion, $D_{L,Taylor}$, is given by [e.g., *Detwiler et al., 2000*]:

$$D_{L,Taylor} = \frac{v^2 b^2}{210 D_0} \tag{1.15}$$

The Taylor dispersion is thus proportional to v^2 and thereby also to Pe^2. A stochastic analysis of the macrodispersion coefficient, $D_{L,macro}$, demonstrates linear proportionality to v and thereby also to Pe. The total longitudinal dispersion in a fracture can then theoretically by described as the sum of

the different dispersion contributions, which in nondimensional form is given by [*Detwiler et al., 2000*]:

$$\frac{D_L}{D_e} = \tau + \alpha_{macro} Pe + \alpha_{Taylor} Pe^2 \tag{1.16}$$

where α_{macro} and α_{Taylor} are nondimensional coefficients for the contribution of Taylor dispersion and macrodispersion, respectively. *Detwiler et al.* [2000] find that for Pe << 1 the dispersion is dominated by molecular diffusion. At intermediate values of Pe the macrodispersion dominates and dispersion will thus depend linearly on Pe ($D_L \propto Pe$). At high Pe values Taylor dispersion will be dominating resulting in a nonlinear relationship between D_L and Pe ($D_L \propto Pe^2$). The dispersion in fractured media and porous media are thus fundamentally different, since a linear dependence of dispersion and v (and thereby Pe) is found in porous media. The differences are caused by the long connected flow paths the fractures constitute, where Taylor dispersion resulting in the nonlinear behavior has more influence than in porous media [*Dullien, 1992; Detwiler et al., 2000*].

The occurrence of both Taylor dispersion and macrodispersion in a fracture can result in different dispersion regimes different places in the fracture system depending on the aperture. Additionally, tracers with different molecular diffusion coefficients can experience different dispersion under the same hydraulic conditions, since the tracers will have different Pe values. However, the interpretation techniques commonly used for tracer tests in fractures incorporate only a dispersion coefficient that is a linear function of velocity, and the effect of Taylor dispersion is thus assumed insignificant.

The dependence on Taylor dispersion may cause anomalous dispersion or so-called non-Fickian dispersion. This deviation from the Fickian behavior has been found in natural geological formations caused by heterogeneities. Commonly two kinds of deviations from the Fickian behavior are encountered: (1) the dependence of the dispersivity on velocity, as described above, and (2) the dependence of the dispersivity on the scale [*Hassanizadeh, 1996*]. The dispersivity dependence on the scale may be very important for fractured systems. Fickian transport will only occur after the solute has traveled a sufficient distance to encounter a statistically significant hydraulic conductivity distribution (in general more than 10 correlation lengths) [*Gelhar et al., 1992*]. For a fractured media the sufficient distance is expected to be large or even infinite because of the heterogeneity in the aperture distribution and Fickian dispersion may thus not fully develop [*Becker and Shapiro, 2000; Manz et al., 1999*].

Matrix diffusion

Another mechanism causing asymmetrical breakthrough curves is the diffusive exchange between fractures and matrix. As described above fractured media can conceptually be divided into a fast flowing domain, the mobile zone, and a no-flow domain, the immobile zone. Diffusive exchange between the two zones is controlled by the local concentration gradient, the molecular diffusion coefficient of the solute, and the porosity and tortuosity of the matrix. The exchange is known as the matrix diffusion and despite its microscopic nature the process can have important implications for large-scale transport and cause severe retardation of solutes in the matrix.

Different formulation and solution methods for matrix diffusion have been suggested. They are all based on Fick's first law and generally use a first-order approximation expressed by [*Haggerty and Gorelick, 1995*]:

$$\theta_{im}\frac{\partial c_{im}}{\partial t} = \alpha\left(c_m - c_{im}\right) \tag{1.17}$$

where α is the first-order mass transfer coefficient [s^{-1}].

The immobile concentration, c_{im}, is the average concentration of the immobile zone and depends on the shape of the matrix block. In general term the immobile concentration is given by [*Haggerty and Gorelick, 1995*]:

$$c_{im} = \frac{\upsilon}{L^{\upsilon}}\int_0^a r^{\upsilon-1}c_r dr \tag{1.18}$$

where c_r is the actual immobile concentration at distance r [kg/m^3], r is the distance form the center of the immobile zone [m], L is the distance from the center to the edge of the immobile zone [m], and υ is the dimensionality of the immobile zone. If υ=1, the immobile zone is composed of layers, if υ=2, the immobile zone is composed of cylinders, and if υ=3, the immobile zone if composed of spheres.

The concentration is determined from the diffusion equation:

$$\frac{\partial c_r}{\partial t} = \frac{D_e}{r^{\upsilon-1}}\frac{\partial}{\partial r}\left[r^{\upsilon-1}\frac{\partial c_r}{\partial r}\right] \tag{1.19}$$

where D_e is the effective diffusion [m^2/s].

The mass transfer coefficient α depends both on the solute and the medium, and involves the diffusion coefficient of the chemical, the length over which the average concentration difference is considered and the cross-sectional area through which the lateral diffusion process takes place. The following relation is found for the first-order mass transfer coefficient [*Parker and Valocchi, 1986; Brusseau et al., 1989*].

$$\alpha = \frac{a}{l^2}D_e\theta_{im} \tag{1.20}$$

where a is a geometric shape factor and l is a characteristic diffusion length [m]. Both parameters depend on the matrix being modeled, e.g., for spherical aggregates a value of 15 is found for the shape factor and the diffusion length is given by the radius of the spheres [*Parker and Valocchi, 1986*].

Analytical solutions of the mobile-immobile fracture model results in an asymptotic dependence of $t^{-3/2}$ for the effluent concentration [*Tsang, 1995; Hadermann and Heer, 1996*]. This implies that breakthrough curves according to the mobile-immobile model will have a tail with a slope of –1.5 in a log-log plot, as long as the outer boundary in the matrix is not influencing the matrix diffusion. At late time, the effluent concentration will decrease rapidly because of the limited matrix volume. Experimental breakthrough curves experiencing the asymptotic –1.5 log-log slope is in general interpreted as evidence of matrix diffusion controlling the transport. However, as described in the following Section 1.7 additional testing may be required.

The influence of matrix heterogeneity on the diffusion process was investigated by *Tidwell et al.* [2000]. They examined the effects of spatially heterogeneous porosity on matrix diffusion using high-resolution X-ray absorption imaging. They used slabs of Culubra dolomite and studied the diffusion of potassium iodide. The acquired images showed significant variations in the diffusion characteristics and these variations were found to be related to the heterogeneous porosity characteristics. These studies suggest that a heterogeneous diffusion characteristic has to be incorporated into modeling of fracture flow. *Haggerty et al.* [1995] developed a multi-rate diffusion model, where a range of diffusion rate coefficients are used to describe the diffusive exchange between the mobile and immobile domain. The model is further described in Section 1.8.1.

The mechanisms described above are based on water being transported along the total fracture plane. As described in Section 1.5.1 channeling in saturated fractures has been observed which will result in stagnant water in the fractures. Thus, diffusion into these stagnant water areas will retard the solutes and result in asymmetrical breakthrough curves. The free-water diffusion is expected to proceed at a rate faster than matrix diffusion, resulting in different values for the observed mass transfer when using the mobile-immobile model. Also inter-channel small aperture spaces in the fracture itself can retard the solute transport. The influence of matrix diffusion on solute transport is traditionally examined by tracer experiments. Difficulties in the interpretation may occur since matrix diffusion will have the same effect of solute transport similar to other mechanisms, like heterogeneity and kinetic sorption [*Carrera et al., 1998*]. However, the different processes can be distinguished by applying multiple tracing methods as described in the following section.

1.6.2 Colloid transport in fractured porous media

Colloids are defined as very fine particles ranging in the size from 10^{-3} to 10 μm including, e.g., clay minerals, metal oxides, viruses, bacteria, and organic macromodules [*Chrysikopoulos and Sim, 1996*]. The study of colloid transport is mainly related to three topics: (1) colloid-facilitated transport of contaminants, (2) transport of pathogens, such as bacteria, viruses, or protozoa, and (3) structure analysis of the subsurface. The main research on colloid transport has been taken place in homogenous porous media, and the knowledge regarding transport in fractured media, and especially in unsaturated fractures, is limited. Transport processes in porous media under both saturated and unsaturated conditions are therefore briefly described below followed by a presentation of transport processes in fractured media.

Colloids in porous media

Field and laboratory experiments in homogenous media have shown that different colloids like bacteria, viruses, inorganic colloids, and polystyrene microspheres can be transported at rates comparable to conservative tracers. Colloid transport, however, differs from solute transport because of colloidal particle interactions like flocculation, mechanical clogging effects, and different surface reactions. The adsorption of colloids onto solid surfaces is traditionally termed deposition, attachment, or filtration. For deposition to happen the colloids have to be transported into the vicinity of the grains. Different mechanisms are responsible for this contact: (1) diffusion (where diffusive Brownian motion transports the colloid towards the grain), (2) straining (where the colloid is retained in a pore smaller than the colloid), (3) interception (where the colloid collides directly with the grain) and (4) sedimentation (where the colloid cannot be kept in

solution). Close to the grain different surface interaction forces including van der Waals attraction, electrostatic repulsion, and chemical and exchange sorption control the deposition on the grains.

The mobility of the colloids has been found to decrease under unsaturated conditions [*Wan and Wilson, 1994*]. The reason for this retardation has been explained by a preferential deposition of the colloids on the air-water interfaces present in unsaturated porous media [*Wan and Wilson, 1994; Corapcioglu and Choi, 1996*]. The sorption of colloids on the air-water interfaces is mainly controlled by the colloid surface hydrophobicity, solution ionic strength, and the particle charge [*Wan and Wilson, 1994*]. The colloid sorption at a static air-water interface is essentially irreversible because of strong capillary forces. Another mechanism suggested to contribute to the increased colloid retention in unsaturated media is film straining [*Wan and Tokunaga, 1997*]. The film straining theory predicts that transport of colloids can only take place if the waterfilm thickness is larger than the colloid diameter, and transport of colloids larger than the film thickness will be inhibited [*Wan and Tokunaga, 1997*].

Colloids in fractured media

Differences in the geometry of water transport conduits cause colloid transport and deposition in fractured media to be significantly different than in porous media. In fractured media colloids have shown to be accelerated compared to solutes, however, a severe retardation have been found, where the effluent show steady peak concentrations considerably below the injection concentration [e.g., *McKay et al. 1993; McKay et al., 2000; Hinsby et al., 1996*].

Different mechanisms are expected to be responsible for the accelerated transport of colloids in fractured media. At small scale a combination of charge exclusion (which will keep the negatively charged colloids in the middle of the fracture), hydrodynamic chromatography (which prevents the colloids from hugging the fracture walls), and Taylor dispersion (which will keep the colloids in the middle because of their small molecular diffusion coefficient) will assure that colloids are mainly transported in the middle of the fractures [*Becker et al., 1999*]. Because of the higher velocity in the middle of the fractures, the velocity of colloids is thereby increased compared to solutes. At large scale, the accelerated transport of colloids compared to solutes is mainly caused by the differences in diffusion. The channeling found in saturated fractured media (Section 1.5.1) will result in stagnant water in the fracture plane, but because of the small molecular diffusion coefficient of colloids, they will spend less time in this stagnant water compared to solutes, and the overall transport velocity is thereby enhanced. Diffusion into the matrix as described for solutes will not have the same influence on the overall transport of colloids. Again this is caused by the small molecular diffusion coefficient of the colloids and also that some colloids are prohibited from accessing the entire matrix pore system because of their large size. Matrix diffusion will thus not retard the transport of colloids in the same manner as seen for solutes.

Severe retardation of colloids has been found experimentally in fractured media, but the processes responsible for this retention are not as well described as for porous media [*Knapp et al., 2000*]. Filtration is one of the explanations suggested for the observed attenuation of colloids during transport in fractures; however, it is unlikely that filtration alone can account for the magnitude of capture [*Becker et al., 1999; Knapp et al., 2000*]. Colloid aggregation is hypothesized to influence the degree of both filtration and settling [*Becker et al., 1999*]. The retention of colloids has shown to depend both on the flow velocity and the colloid size [*Cumbie and McKay, 1999*]. In fractured

shale an optimum colloid size of ~0.5 μm was found, i.e. this colloid size resulted in the highest relative concentration and the greatest cumulative recovery [*Cumbie and McKay, 1999*]. Colloids smaller than the optimum size were more retarded because of higher diffusion into the matrix and other immobile pore water regions, whereas colloids larger than the optimum size experienced a higher retention because of gravitational settling and straining in small aperture regions.

To the author's knowledge only few experiments have examined transport of colloids in unsaturated fractures. Based on the results found for unsaturated porous media, where irreversible sorption to the air-water interfaces increased the retardation of colloids, a similar mechanism is hypothesized to exist in unsaturated fractures. *Ullum* [2001] examined the transport of colloids in artificial macropores under unsaturated conditions; however, problems activating the macropores under the current experimental setup limited the general applicability of the experimental results. *Mortensen et al.* [2001b] performed multiple tracing experiments in unsaturated fractured clayey till and applied colloids as tracers. The results from this experiment are presented in Part 3 and summarized in Section 1.7.4.

Several researchers have applied colloids as tracer in fractured media, since they provide additional information on the soil structure than obtained from traditional solute tracers. The application of colloidal tracers in fractured media is further described in Section 1.7.2, and a brief description of colloid modeling is given in Section 1.8.5.

1.7 Tracer experiments in fractured media

Tracer experiments, where one or several tracers are introduced to the area of interest, is a common technique for studying flow and transport in porous and fractured media. Breakthrough curves obtained at observation well or outlets downstream will provide information on the structure and chemical properties of the medium. In homogeneous porous media, tracer experiments with one conservative tracer are traditionally performed to obtain information on pore water velocity and dispersion. In fractured media, the nonideal transport of solutes as described above will limit the interpretation of a traditional tracer test with only one tracer. When only applying one tracer, matrix diffusion cannot be distinguished from heterogeneity and kinetic sorption that both will result in asymmetrical breakthrough curves [*Carrera et al., 1998*]. To avoid these problems of nonuniqueness, multiple tracing techniques have become common in fractured media.

Multiple tracing techniques are applied to reveal nonequilibrium processes resulting from the time-dependent mass exchange between the mobile and immobile domains. Different techniques have been applied where the most common at field scale are: (1) using multiple tracers with different diffusion coefficients, (2) using multiple tracers with grossly different sizes, (3) performing tracer test with different flow rates, and (4) isolating the diffusion processes with flow interruption [*Jardine et al., 1999; Becker and Shapiro, 2000, Carrera et al., 1998*].

The different techniques are briefly presented below, including a description of the most common conservative tracers used in fractured media. In Section 1.7.4 examples of experiments applying these multiple tracing techniques are presented.

1.7.1 Multiple tracers with different diffusion coefficients

The application of multiple solute tracers takes advantage of the differences in the molecular diffusion coefficient among the applied tracers. If diffusion takes place into immobile regions, like stagnant water in the fracture plane or into the surrounding matrix, differences in breakthrough for the different tracers are expected. Thus tracers with high diffusion coefficients will be transported further into the immobile regions and thereby be more retarded compared to solutes with small diffusion coefficients. The result will be differences in the breakthrough curves, where tracers with high diffusion coefficients will show smaller peak concentration and a more prolonged tailing compared to solutes with small diffusion coefficients. However, differences in diffusivity also imply differences in accessible porosities, which may have influence on the obtained breakthrough curves [*Carrera et al., 1998*].

The multiple tracing techniques have been applied in different media and at different scales [e.g., *Jardine et al., 1999, Maloszewski et al., 1999, Callahan et al., 2000, Becker and Shapiro, 2000; Meigs et al., 2001, and Mortensen et al., 2001b*]. The technique is traditionally applied using different conservative tracers, but a mixture of conservative and reactive tracers can be applied as well. Different solute chemicals are suitable as groundwater tracers, and the most common will be presented below, with focus on conservative tracers.

Solute tracers

Different conservative tracers have been applied in fractured media. These include inorganic ions from common salts (e.g., bromide and chloride), organic ions (e.g., fluorobenzoic acids), dyes (e.g., uranine), gasses (e.g., helium and neon), and stable isotopes (like tritium and deuterium).

Inorganic anions, in the form of common salts, are often applied as groundwater tracers because of their stability and low susceptibility of sorption onto groundwater media [*Davis et al., 1985*]. The most common tracers are bromide (Br^-) and chloride (Cl^-). Chloride can, however, experience high background levels, which will limit its use because density driven flow may have influence on the transport when applying high concentrations. Iodide (I^-) is also commonly used as tracer, but tends to be sorbed more than bromide and chloride [*Davis et al., 1985*]. A general drawback of the anion tracers is that anion exclusion in negatively charged media like clay will enhance the velocity of the tracers.

A group of organic anions, the so-called fluorobenzoic acids, have recently been applied as groundwater tracers [e.g., *Dahan et al., 1999; Becker and Shapiro, 2000*]. The fluorobenzoic acids are a group of 16 isomers (see Table 1.1). Many of these isomers have features that make them suitable as groundwater tracers: (1) they are detectable at low concentrations, (2) they are nonreactive in groundwater, and (3) the different isomers can be distinguished from each other and from naturally occurring ions [*Bowman and Gibbens, 1992; Benson and Bowman, 1994*]. Another advantage is that the isomers have approximately the same diffusion coefficient in water (see Table 1.1). This is useful when repeating tracer experiments with different flow properties and several tracers with the same diffusion characteristics are needed.

McCarthy et al. [2000] examined the sorption of four different fluorobenzoic acids in highly weathered and fractured clay-rich saprolite at different pH. For fluorobenzoic acids the ratio of the non-ionized and anionic forms is dependent on the solution pH and the pK_a of the individual

isomer. At pH < pK_a, the protonated non-ionized form of the FBA dominates, while the anionic species begins to dominate at pH > pK_a. Only the anionic species is usually nonreactive and the use of fluorobenzoic acids as conservative tracers thus depends on the pH and the pK_a. The experiments by *McCarthy et al.* [2000] show that fluorobenzoic acids can be considered nonreactive in saprolite as long as the pH is approximately 2 pH units above the pK_a.

Table 1.1. Aqueous molecular diffusion coefficient D_0 (298 K) and negative log acid dissociation constants pK_a (298 K) for the isomers of fluorobenzoic acid [*Bowman and Gibbens, 1992; Benson and Bowman, 1994*].

Compound	D_0 ($m^2/s \times 10^{-10}$)	pK_a
2,3-DFBA	7.6	3.29
2,4-DFBA	7.6	3.58
2,5-DFBA	7.6	3.3
2,6-DFBA	7.6	2.85
3,4-DFBA	7.6	3.83
3,5-DFBA	7.6	3.59
2,3,4-TFBA	7.5	3.30
2,3,6-TFBA	7.5	2.82
2,4,5-TFBA	7.5	3.28
2,4,6-TFBA	7.5	2.83
3,4,5-TFBA	7.5	3.54
2,3,4,5-TEFBA	7.4	3.08
2,3,5,6-TEFBA	7.4	2.71
PFBA	7.2	2.72
m-TFMBA	7.4	3.8
o-TFMBA	7.3	3.0

DFBA–difluorobenzoate; TFBA–trifluorobenzoate; TEFBA–tetrafluorobenzoate; PFBA–pentafluorobenzoate; TFMBA–trifluoromethylbenzoate.

Some of the fluorobenzoic acids (especially m-TFBA and o-TBFA) have exhibited a tendency to degrade under unsaturated condition. Based on their reliability as stable, nonreactive, anionic tracers the following ranking is found: PFBA>2,6-DFBA>2,3-DFBA=2,5-DFBA=3,4-DFBA=3,5-DFBA>o-TFMBA> m-TFMBA [*Bowman and Gibbens, 1992*]. The toxicity of fluorobenzoic acid is a concern when applied as groundwater tracer. The aquatic toxicity of different fluorobenzoic acid was assessed by *McCarthy et al.* [2000] using Ceriodaphnia 96-h acute toxicity test. The LD50 (the concentration resulting in mortality of ≥ 50% of the test organisms) was above 100 mg/L for the four fluorobenzoic acid isomers tested.

Another group of chemicals commonly applied as groundwater tracers are dyes. The fluorescent dyes are the most common group used as tracers since they are easy to detect even at low levels. The fluorescent tracers can be classified into three groups: (1) dyes with green to red fluoresce (e.g., uranine, eosin and rhodamine), (2) dyes with blue to green fluoresce (e.g., pyranine and sodium napthionate), and (3) dyes with blue fluoresce the so-called optical brighteners (e.g., tinopal CBS-X) [*Käss, 1998*]. The majority of the fluorescent dyes sorbs to sediments and aquifer media and cannot be considered as conservative tracers. Several researchers have performed sorption experiments with fluorescent dyes on different materials, but with varying results. *Kasnavia et al.*

[1999] examined the sorption of the four most common fluorescent dyes (uranine, rhodamine B, rhodamine WT, and sulforhodamine B) on different mineral surfaces. Uranine (also known as fluorescein) has anionic functional groups and showed least sorption onto negatively charged media. The rhodamine dyes have both cationic and anionic functional groups and are thus more susceptible to sorption. The sulforhodamine B dye showed least sorption of the examined rhodamine dyes. Sorption of uranine was also observed by *Sabatini and Austin* [1991] on alluvial sand, and by *Maloszewski et al.* [1999] on rock materials, whereas *Käss* [1998] concludes that uranine behaves conservatively, even in clay materials.

The intensity of the fluorescence are sensible to several factors, including pH, temperature, turbidity, chloride content, and decomposition due to light [*Käss, 1998*]. Especially the fluorescence of uranine is sensitive to the pH value (see Figure 1.2); however, the dependence is reversible. Examples of the multiple tracing techniques with different solutes are presented in Section 1.7.4.

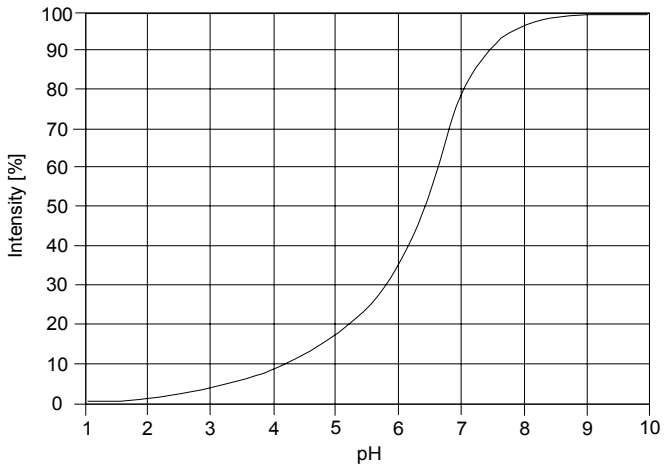

Figure 1.1. Dependence of the intensity of uranine's fluorescence upon the pH value [from *Käss, 1998*].

1.7.2 Multiple tracers with different sizes

Another common multiple tracing technique in fractured media takes advantage of the differences between transport of solutes and colloids. As described in Section 1.6.2, colloids are transported faster through the fractures and will not be exposed to matrix diffusion at the same level as solutes. The use of colloids and solutes at the same time can thereby provide additional and complementary information on the media structure and the nonideal transport processes. Additionally, the colloid tracer can be used to examine the influence of colloid-facilitated transport or transport of different pathogens.

Different types of colloids have been applied as tracers in fractured media, including bacteria, bacteriophages, and fluorescent latex microspheres. The use of bacteria and bacteriophages is traditionally a cheap method, but degradation during the experiments has to be taken into account. The fluorescent latex microspheres are attractive as colloid tracers because they are perfectly spherical, resistant to biodegradation, stable at normal temperatures, and commercially available in different sizes and colors. Different techniques are available for detecting fluorescent colloids including fluorometers, flow cytometers, and manual counting in fluorescent microscope.

When applying colloids as tracer the influence of flow rate and colloid size on the retention has to be taken into account. Different colloids, like bacteria, bacteriophages or microspheres will have different size and thereby differ in transport processes. As described in Section 1.6.2 small colloids will be retarded because of diffusion into the matrix and other immobile pore water regions, whereas large colloids will be retarded because of an increased gravitational settling and straining in small aperture regions.

By comparing solute and colloid transport differences in the diffusion processes are revealed. However, the significant retardation of colloids complicates a quantitative analysis of the colloid transport. Examples of colloids and solutes as tracers in fractured media are presented in Section 1.7.4.

1.7.3 Changes in fluid properties

Since diffusion processes are time-dependent a change in fluid properties will induce a change in diffusion processes. This can either be done by repeating tracer experiments at different flow rates or by using flow interruption during the experiment. When repeating a tracer experiment, large differences in velocity are advisable, since this will increase the differences in the breakthrough curves. Additionally, by performing one of the experiments with a very low velocity the chance of the diffusion processes to have influence on the transport is enhanced. Tracers with the same characteristics should be used in the two experiments; either by applying the same tracer in both experiments, if background concentrations can be neglected, or by applying two tracers with the same characteristics, like for example the fluorobenzoic acids as described in Section 1.7.1.

Instead of repeating an experiment, the diffusion processes can be isolated by using flow interruption. The technique consists of inhibiting the flow process during the tracer experiment for a designated amount of time and thereby allow a new physical or chemical equilibrium state to be approached [*Reedy et al., 1996*]. After resuming the flow, an eventual diffusion process will result in a change in the outflow concentration. The technique can thus be used to confirm and quantify the significance of diffusion to the overall physical nonequilibrium mechanism. The technique is mainly used at saturated conditions at laboratory or lysimeter scale, where flow control is possible [e.g., *Hu and Brusseau, 1995; Reedy et al., 1996, Cote et al., 2000*].

The effect of the flow interruption depends on several factors, including the flux of the experiment, the length of the interruption, and when during the experimental period the flow interruption takes place [*Reedy et al., 1996*]. If the flow interruption takes place during tracer injection, the outflow concentration will decrease after resuming the flow assuming diffusion processes have influence on the transport. This is caused by the concentration gradient from the large conductive fractures into the small pores in the matrix. If the flow interruption, however, takes place during the tracer displacement (the washout period) the outflow concentration will increase after resuming the flow. During the washout period the diffusion gradient will result in transport from the matrix and into the fractures now containing clean water. If the flow interruption takes place in an experiment with high flow velocity a more pronounced concentration perturbation is seen. This is because the system is further removed from equilibrium at the larger fluxes, and a greater concentration gradient will thereby exist between advection-dominated flow paths and the soil matrix [*Reedy et al., 1996; Jardine et al., 2000*]. A long flow interruption will also result in a larger concentration perturbation, since the concentration gradient is allowed to more closely approach equilibrium.

Cote et al. [2000] examined the leaching from an aggregated soil during flow interruption, where the preferential flow paths were allowed to drain during the interruption. They found that the leaching increases when using flow interruption. They concluded that the concentration gradients even out within the undrained region during the flow interruption, so that upon resuming the flow, solute exchange is enhanced. The longer the flow interruption, and thereby longer drainage period applied, the more efficient leaching is expected because of the additional time to even out the concentration.

Examples of applying changes to the flow properties, either by performing several tracer tests with different flow velocities or by using flow interruption are presented below.

1.7.4 Application of multiple tracing techniques

Application of multiple tracing techniques has recently become the common method when performing tracer experiments in fractured media. One or several of the methods presented above are applied in the experimental procedure to reveal non-ideal transport processes; however, the results obtained are not always clear, revealing limitations in the current understanding of flow and transport processes in fractured media. Examples of tracer experiments in fractured media where multiple tracing techniques are applied are presented in this section.

Using multiple tracers with different diffusion coefficients is an easy and very common method for examining nonequilibrium processes in fractured media. *Jardine et al.* [1999] performed a long-term, near steady state natural gradient injection of multiple tracers in fractured shale bedrock. Three nonreactive tracers He, Ne, and Br with different molecular diffusion coefficients were applied. Concentrations were measured at several positions downstream, both inside the matrix and in the fractures. Close to the source, the movement of He and Ne in and out of the matrix was more rapid than Br, as is consistent with the larger molecular diffusion coefficients of the dissolved gases relative to Br. The application of a multiple tracer technique thus confirmed that matrix diffusion was a significant process that contributed to the overall physical nonequilibrium controlling contaminant transport in the shale bedrock. However, they also noted that it was important to perform a long-term, steady-state, natural gradient injection to be able to observe the tracer migration into the matrix.

Callahan et al. [2000] applied several multiple tracing techniques to examine the effects of matrix diffusion in fractured volcanic rock. In an intact core, an artificial fracture was created and used for studying solute transport. The experiments included a multiple tracing experiment with bromide and PFBA as tracers and with a 20-hour flow interruption at late time, and several experiments at different flow rates with iodide as tracer. The breakthrough curves obtained all showed a –1.5 log-log slope, which in general is considered evidence for diffusive mass transfer as described in Section 1.6.1. Differences in the breakthrough revealed that the mass transfer between fracture and matrix was found to be dependent on: (1) fracture residence time, since different flow rates showed different results, (2) molecular diffusion coefficient, since Br and PFBA showed different results, and (3) matrix permeability, since different cores showed different results. Diffusion cell experiments were performed as well, and matrix diffusion coefficients for Br and PFBA were calculated and compared with the corresponding values determined from the fracture core experiments. The results from the fracture core experiments were ~2 times greater then calculated based on the diffusion cell experiments. The main causes for the differences were hypothesized to

be: (1) larger surface areas in the fracture core, because of fracture roughness (parallel plate was assumed in the calculations), and (2) solute diffusion into stagnant water in the fracture, because of heterogeneity and channeling.

Becker and Shapiro [2000] also applied multiple tracers to investigate the reasons for nonequilibrium tracer breakthrough, but the results obtained did not show the expected differences. They performed a weak dipole tracer experiment in crystalline rock using the conservative tracers HDO (deuterated water), Br, and PFBA with variable diffusion coefficients. Given the low porosity of the rock matrix (<2%) and the limited duration of the tracer tests, they did not expect that a significant amount of tracer would diffuse into the matrix. However, the obtained breakthrough curves were asymmetrical and showed an early peak and an extended breakthrough tailing with an approximately slope of –2 in a log-log plot. Several multiple tracing techniques were applied to evaluate the influence of nonequilibrium. Breakthrough curves obtained using different tracers were indistinguishable, and also experiments performed at different pumping rates, all with bromide as tracer, showed no significant differences in the obtained breakthrough. They concluded that the observed breakthrough tailing was independent of the flow rate and the molecular diffusion coefficient and that a more complex dispersive mechanism dominated the transport in the reported tests. Non-Fickian dispersion was implied as a possible explanation for the extended tailing, but the only way to confirm this hypothesis was to repeat the test between wells with different distances, which was not conducted in the current study.

McKay et al. [2000] applied colloidal and solute tracers in a field scale tracer experiment in saturated fractured shale saprolite. The colloidal tracers were found to arrive before the solute tracers and the difference between tracer arrival time increased with the distance from the source. The colloidal tracers showed transport velocities up to 500 times faster than the solute tracers, and the differences were explained by the greater diffusion of solute tracers into the matrix. The colloid retention were found to depend both on the size of the colloid and the travel distance.

Flow and transport in unsaturated fractured clayey till was examined by *Mortensen et al.* [2001b]. Only a few experiments have examined the effect of preferential flow in unsaturated fractured clay because of the difficulties in monitoring and sampling. Experiments have included small-scale laboratory experiments on undisturbed soil monoliths [e.g., *Wildenschild et al., 1994*], intermediate scale lysimeters [e.g., *Vink et al., 1997; Schoen et al., 1999*] and dye-tracer experiments [e.g., *Forrer et al., 2000; Stadler et al., 2000*], and large-scale tile-drain experiments [e.g., *Villholth et al., 2000*]. The different approaches each have limitations regarding characterizing flow and transport in fractured media. The column and lysimeter experiments are both limited in scale, the dye experiments fail to characterize the speed of the preferential flow, and the tile-drain experiments fail to provide spatial resolution. Highly controlled tracer experiments were performed by *Mortensen et al.* [2001b] in an isolated block of clayey till with the dimensions 3.5m x 3.5 m and 3.3 m deep at Avedøre, Denmark. The set-up allowed full control of the water balance, where an automatic watering device applied different constant water intensities to the block surface and horizontal drainpipes at 3.3 m depth were used for drainage. A constant water level was maintained 0.3 m above the block floor leaving 3 m unsaturated zone above. Retention characteristics of the clay showed that the matrix could be expected to be fully saturated throughout the experimental period, and only fractures and macropores in the top 3 m varied in saturation depending on the applied water intensity.

Four experiments were conducted with a constant water intensity of 4 mm/h, 6.2 mm/h or 9.6 mm/h, respectively. Multiple tracers with different diffusion coefficients were applied, including bromide, chloride, 2,6-DFBA, 2,3-DFBA, uranine, and sulforhodamine B, so that in each experiment one anion, one fluorobenzoic acid, and one fluorescent dye were applied. Additionally, latex colloids were applied as a colloidal tracer in the 4 mm/h experiment. Based on the work by *Cumbie and McKay* [1999] colloids with the size of 0.5 μm was chosen, since this size was found to be optimum for transport in shale saprolite, a material similar to the clayey till found at the Avedøre field site. Flux averaged breakthrough curves for the entire block were obtained at 3.3 m depth by monitored the concentration of the effluent water from the horizontal drainpipes.

The breakthrough curves obtained at the three different water intensities showed large mutual differences. At high water intensities, asymmetrical breakthrough curves were obtained where the solute concentration peaked early and was followed by a long tailing period. The multiple tracers applied in each experiment only showed small differences in breakthrough. The fluorobenzoic acids peaked slightly earlier than the anions and with a higher peak concentration, which is consistent with the smaller diffusion coefficient of the fluorobenzoic acids. The 4 mm/h experiment was conducted with two pulse durations. First a 10 minute tracer pulse was applied, however, the tracers were not detectable in the effluent water, either because of retardation by diffusion or because the effluent concentrations were below the detection levels. By applying a 120-minute pulse, the tracers were detectable in the effluent water. The breakthrough curves for both bromide and 2,3-DFBA showed double peaks, whereas uranine had a traditional one-peak behavior. The double peak was interpreted to be caused by severe matrix diffusion. This will retard the solutes and result in a small peak followed by a longer more smeared peak during the wash-out period. Uranine did not show the double peak behavior, which corresponds with its smaller diffusion coefficient compared to bromide and 2,3-DFBA. However, the peak concentration was lower than expected, which suggest that sorption of uranine to the clay matrix may have influenced the measured breakthrough curve.

The differences between the breakthrough of the colloid tracer and the solutes showed the importance of solute size on the transport processes in fractures. The colloids were severely retarded compared to the solutes because of filtration and likely also sorption onto air-water interfaces. However the colloid breakthrough peaked earlier than found for the solutes indicating higher transport velocities. The colloid concentration declined quickly after the peak and did not show the double peak behavior as seen for the solutes. The cause was interpreted to be differences in diffusion into stagnant areas which both explain the faster transport of the colloids compared to the solutes and the missing double peak in the breakthrough curve.

The multiple tracing techniques gave results that both supported and contradicted with the behavior expected for a mobile-immobile medium. Differences between colloids and solutes in the 4 mm/h experiment suggest that diffusive exchange between fractures and matrix is an important process. However, larger differences between bromide and 2,3-DFBA were expected as well. At high water intensities, only small differences between the multiple tracers were seen, which might be because the diffusive processes are not important for the transport. The observed asymmetrical breakthrough might instead be caused by heterogeneity in the fractures or near the bottom boundary. Nevertheless, the experiments at Avedøre show that solutes can be transported very fast

through unsaturated fractured clayey till during steady-state conditions. The next interesting aspect would be to examine the influence of transient water intensities on the transport.

Examples of dual-porosity modeling of the experimental results are presented in Section 1.8.6.

1.8 Modeling of flow and transport in fractured media

Numerous researchers have applied numerical flow and transport models to fractured systems, and several different modeling approaches has been proposed. The most common approaches can be divided into the following categories: (1) continuum models, (2) discrete fracture network models, and (3) hybrid models. The continuum models include single continuum, effective continuum, and dual continua models and are the most commonly applied approach because of its simplicity. The discrete fracture network models simulate the fractures explicitly; and the hybrid models are based on an intermediate approach, where the continuum approach is combined with the discrete fracture network model.

The decision of which model is the most appropriate depends on the characteristics of the system being considered. Some of the factors that need to be taken into account include: (1) the scale of the problem, (2) the amount of data available, (3) the fracture characteristics (e.g. connectivity, spacing, and aperture), and (4) the matrix characteristics (e.g. permeability and block size). Additionally, the purpose of the model simulations has to be taken into account, e.g. if a complete understanding and accurate reproduction of all features are not required a more simple model approach might be sufficient. Whether fractures need to be explicitly incorporated in the numerical model depends on the relation between the scale of the fractures and the scale of the model [*Doughty, 2000*]. In small-scale experiments focused on a few individual fractures, explicit representation of the fractures including aperture distribution in a discrete fracture network model might be desirable. At large-scale, more fractures have to be incorporated into the model, which can be done either by a stochastic description or by using one of the continuum approaches. Finally, the hybrid models might be useful to incorporate different scales of heterogeneity.

In the following the different model approaches are briefly presented, first for saturated conditions and in Section 1.8.4 for unsaturated conditions. The description will focus on dual-continua models, and examples of dual-continua applications are presented in Section 1.8.6.

1.8.1 Continuum models

Continuum models are commonly applied to fractured porous media because of their simplicity. The continuum models are based on volume averaging that assumes that processes in both fractures and matrix can be described within a representative elementary volume (REV) of the formation. The heterogeneity of a fractured media is thus modeled by using a limited number of regions, each with uniform properties. Within the continuum, local thermodynamic equilibrium is assumed, which require that temperature, phase pressure, densities, viscosities, enthalpies, and component concentration are the same locally at any REV of the formation [*Wu, 2000*]. At the scale of interest hydraulic properties are represented by coefficients, such as permeability and porosity, that express the volume average behavior [*National Research Council Committee on Fracture Characterization and Fluid Flow, 1996*]. Commonly the models are deterministic, but also stochastic continuum models are used where the coefficients are characterized by a probability distribution.

The modeling approach is well suited for representing large-scale geological features. The two greatest limitations are (1) the scale at which the continuum approximation is justified can be difficult to quantify and may in fact not be justified at any scale and (2) the process of spatial averaging restricts the model predictions to scales greater than or equal to that of the REV [*National Research Council Committee on Fracture Characterization and Fluid Flow, 1996*]. The concept of the REV may thus be irrelevant to most field measurements, and especially in fractured media, a REV can be difficult to define [*National Research Council Committee on Fracture Characterization and Fluid Flow, 1996*].

The continuum models are divided into three different groups: (1) single continuum models, (2) effective continuum models and (3) dual continua models. The single continuum and effective continuum models both treat the fractured medium as one continuum. The dual continua models use two overlapping continua to represent fracture and matrix, respectively. Different approaches to describe the matrix result in the following four different dual-continua concepts: dual-porosity, dual-permeability, and multiple interacting continua (also known as MINC) for both the dual-porosity and the dual-permeability concepts. The different approaches are presented schematically in Figure 1.2 and will briefly be presented below. Note that in the literature, different grouping and naming of the modeling approaches can be found. In the present report, the definitions are based on the most recent literature, e.g. *National Research Council Committee on Fracture Characterization and Fluid Flow* [1996], *Pruess et al.* [1999], and *Doughty* [1999].

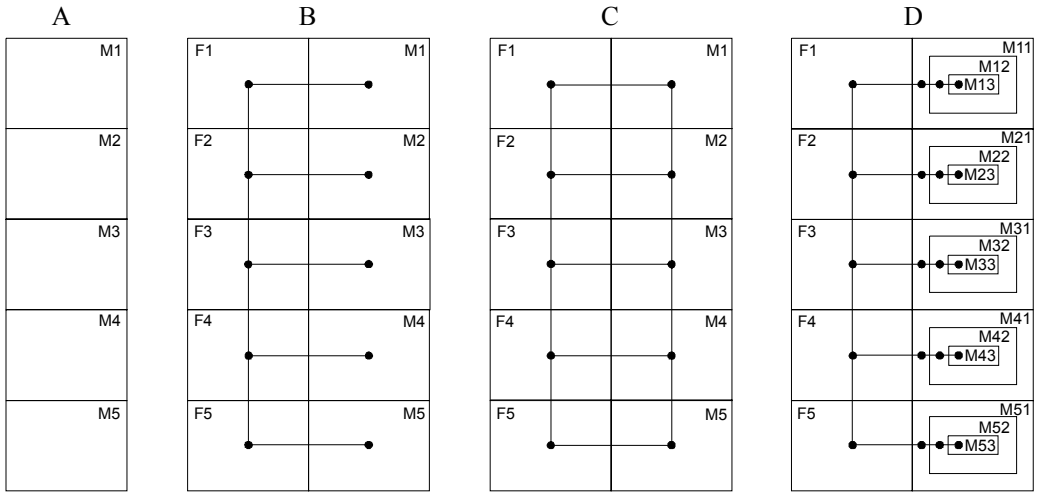

Figure 1.2. Schematic diagram of a 1-D column with gridblocks modeled as (A) single continuum or effective continuum, (B) dual-porosity, (C) dual-permeability, and (D) multiple interacting continua (here shown as a dual-porosity model) [from *Doughty, 1999*].

Single continuum models

The simplest approximation when modeling fracture flow and transport is representing the fractured media as a single continuum. Depending on the desired setup, the single continuum model can be used to represent just the matrix or more common just the fracture network. A single continuum approach only representing the fracture network is a simple alternative model that may provide insight into simple steady-state flow problems [*Doughty, 1999*]. The assumption is, however, that the matrix permeability is sufficient low to ensure that fracture-matrix exchanges can be neglected. Recently, stochastic continuum models have been applied, where the heterogeneity of

the flow field in the fractured network is generated stochastically [*National Research Council Committee on Fracture Characterization and Fluid Flow, 1996; Birkholzer et al., 1999*].

A more common application of the single-continuum approach is to use effective parameters to present both the fractures and the matrix. This approach is known as the effective continuum model and is described below.

Effective continuum models

The effective continuum model (ECM) represents both the fractures and the matrix in each gridblock (see Figure 1.2), and flow and transport are described as in the single-continuum model by using effective parameters. The advantage of the ECM approach is that it does not require detailed knowledge of the fractured media, like distributions and interface areas of fractures and matrix geometric properties. The ECM thus provides a simple, alternative conceptual model and is commonly applied to fracture-matrix flow problems [e.g. *McKay et al., 1997*]. The assumption of applying ECM is that approximate thermodynamic equilibrium locally exists between fractures and matrix at all times, which is equivalent to assuming that fracture-matrix flow occurs instantaneously [*Doughty, 1999; Wu, 2000*]. The likelihood of the ECM approach being appropriate thus increases the faster the fracture-matrix exchange takes place. This has led to the following characteristics of a medium suitable for ECM: (1) high fracture density, which creates connected fractures, (2) relatively constant fracture aperture, to prevent that only a few fractures control the main part of the flow, (3) random orientation of fractures, to prevent flow from only taking place in one direction, and (4) relatively small matrix blocks with high permeability [*Long et al., 1982; Wu, 2000*]. Additionally, the larger the scale the more realistic results for the ECM approach will in general be obtained.

Several researchers have investigated the accuracy and applicability of the ECM to field problems and *Wu* [2000] concludes that the ECM is adequate for modeling steady-state flow as long as there are strong fracture-matrix interactions. If strong nonequilibrium exists between fracture and matrix the ECM approximation will introduce errors. However, the ECM can be a useful tool to obtain initial conditions for subsequent dual-permeability simulations. In situations where no detailed fracture characteristics are available the use of more complex modeling approaches (like the dual-permeability or other multi-continua model) will likely not give better results than a simple ECM model because of the uncertainty in fracture and matrix data. However, the limitations for applying the ECM approach as described above must be recognized and examined before use.

Dual continua models

The most common modeling approach for fractured porous media is the dual-continua model (DCM) [*Wu, 2000*]. Here the fractured medium is characterized as two overlapping continua that are both treated as a porous media. Each gridblock is thus subdivided into a fracture block and one or more matrix block (see Figure 1.2). Unlike the ECM, these gridblocks need not be in thermodynamic equilibrium, so finite fracture-matrix flow rates can be represented [*Doughty, 1999*].

The dual-continua models can be divided into the so-called dual-porosity and dual-permeability models (see Figure 1.2). If flow only occurs between the fracture gridblocks the model is known as a dual-porosity model. Flow in the matrix is thus neglected and the matrix only contributes as an

additional storage term. If flow occurs both within the fracture and the matrix, the model is known as a dual-permeability model. Flow and transport are then described using separate flow and transport equations for fracture and matrix, respectively.

The dual-porosity model (also known as the mobile-immobile model) is the most commonly applied model in fractured media, since matrix flow often is negligible compared to the fracture flow. In the classical dual-porosity model, matrix is represented as a periodic array of identical blocks completely surrounded by fractures [*Warren and Root, 1963*]. *Pruess and Narasimhan* [1985] modified the dual-porosity approach to include multiple-interacting continua (MINC), where each matrix block is discretized into multiple nodes (see Figure 1.2). Variably properties can thereby be assigned to each matrix block allowing for local gradients to be present. The MINC approach may describe field-processes more closely than the traditional dual-porosity model, but a greater number of parameters for model calibration are also required [*Ray et al., 1997*].

Solute transport between fracture and matrix in the dual-porosity model is controlled by diffusion. As described in Section 1.6.1 different approaches for handling matrix diffusion are available, where the most common approaches are based on first-order mass transfer models. An example of a dual-porosity model is CXTFIT [*Toride et al., 1995*]. The model is a mobile-immobile two-region model with linear sorption (note that first-order degradation and zero-order production can be modeled as well, but is not described here). The two-region solute transport equation is given by [*Nkedi-Kizza et al., 1984*]:

$$\left(\theta_m + f\rho_b K_d\right)\frac{\partial c_m}{\partial t} + \left[\theta_{im} + \left(1-f\right)\rho_b K_d\right]\frac{\partial c_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - \theta_m v_m \frac{\partial c_m}{\partial x} \tag{1.21}$$

$$\left[\theta_{im} + \left(1-f\right)\rho_b K_d\right]\frac{\partial c_{im}}{\partial t} = \alpha\left(c_m - c_{im}\right) \tag{1.22}$$

where index m and im refers to the mobile and immobile domain, respectively, c is the concentration [kg/m^3], t is the time [s], θ is the volumetric water content, f is the fraction of sorption sites which is in direct contact with the mobile liquid, ρ_b is the bulk density [kg/m^3], K_d is the equilibrium sorption coefficient [m^3/kg], D is the dispersion coefficient [m^2/s], v is the velocity [m/s], and α is the first-order mass transfer coefficient [s^{-1}]. Written in dimensionless variables the transport equation is given by:

$$\beta R\frac{\partial C_m}{\partial T} + \left(1-\beta\right)R\frac{\partial C_{im}}{\partial T} = \frac{1}{P}\frac{\partial^2 C_m}{\partial Z^2} - \frac{\partial C_m}{\partial Z} \tag{1.23}$$

$$\left(1-\beta\right)R\frac{\partial C_{im}}{\partial T} = \omega\left(C_m - C_{im}\right) \tag{1.24}$$

where the dimensionless parameters are defined as follows:

$$C_m = \frac{c_m}{c_0} \quad ; \quad C_{im} = \frac{c_{im}}{c_0} \tag{1.25}$$

$$T = \frac{vt}{L} \quad ; \quad Z = \frac{x}{L} \tag{1.26}$$

$$\phi_m = \frac{\theta_m}{\theta} \quad ; \quad \theta = \theta_m + \theta_{im} \tag{1.27}$$

$$P = \frac{vL}{D} \quad ; \quad D = D_m \frac{\theta_m}{\theta} \tag{1.28}$$

$$\omega = \frac{\alpha L}{v\theta} = \frac{\alpha L}{q} \quad ; \quad q = v\theta = v_m\theta_m \tag{1.29}$$

$$\beta = \frac{\theta_m + f\rho_b K_d}{\theta + \rho_b K_d} \tag{1.30}$$

$$R = 1 + \frac{\rho K_d}{\theta} \tag{1.31}$$

where c_0 is the input concentration [kg/m^3], L is a characteristic length [m], ϕ_m is the fraction of mobile water, P is the Peclet number, ω is a dimensionless mass transfer coefficient (the Damkohler number), and R is the retardation factor. Note that for a conservative solute (K_d=0), β, equals the fraction of mobile water, ϕ_m. The Damkohler number, ω, contains the first-order mass transfer coefficient, α, and represents the mass transfer of solutes between the mobile and immobile domains. The coefficient associated with the first-order model can be related to the molecular diffusion coefficient, based on the Fick´s law approach, as presented in Equation 1.20.

Haggerty and Gorelick [1995] modified the dual-porosity model and applied a multi-rate diffusion model, where diffusion of mass from the mobile and immobile domain is described by a range of diffusion rate coefficients. Variability in the diffusion rate is due to a combination of factors, including variability in at least the following: (1) matrix block size, (2) tortuosity, (3) pore geometry, (4) restricted diffusion within pores (i.e., diffusion is slowed by small cross sectional area of the pore), (5) variably sized dead-end pores adjacent to the advective porosity, and (6) interaction with the pore walls, including sorption. Because the diffusion rate coefficient is the product of several parameters that each has variability, a lognormal distribution is assumed [*Haggerty et al., 2001*].

Dual-permeability models are applied to fractured systems when matrix flow cannot be neglected [e.g., *Birkhölzer et al., 1993*]. Flow and transport are then described by separate flow and transport equations for the fracture and matrix pore system, respectively. Crucial to application of a dual-permeability model is thus the need for independent determination of a dual set of soil hydraulic properties and transport parameters [*Vogel et al., 2000*]. As described for the dual-porosity models a multiple interacting continua (MINC) approach can be used for discretizing the matrix blocks into several nodes, thereby allowing for a transient description of fracture-matrix flow [*Doughty, 1999*]. Dual-permeability models are more commonly applied to unsaturated fractured systems to describe flow and transport into the matrix. The application of dual-permeability models is further described in Section 1.8.6.

Limitations of the dual-porosity and dual-permeability models have been found by several researchers. The main problems with these models are (1) they overregularize the geometry of the fracture network, and (2) good parameter estimates are difficult to obtain [*National Research Council Committee on Fracture Characterization and Fluid Flow, 1996*]. However, since the dual-continua models are conceptually appealing and computationally much less demanding than the discrete fracture network models as described below, they are still the main approach in handling fluid flow, heat transport and chemical transport through fracture-matrix systems [*Wu, 2000*].

1.8.2 Discrete fracture network models

An alternative approach to continuum models is the discrete fracture network models. Two different types of discrete fracture network models are found – the ones that only represent the fracture network, and thereby neglect exchange of fluid and solutes with the matrix, and the ones that represent both the fracture network and the surrounding matrix. The traditional discrete fracture network model assumes the matrix to be impervious. A stochastic generation of the fracture network thus describes the natural fracture system statistically. For each fracture or fracture set the following data are normally acquired to build a fracture network: (1) fracture location, (2) fracture orientation, (3) fracture trace length, (4) percentage of fractures that terminate against other fractures, (5) estimates of the transmissivity of individual fractures [*National Research Council Committee on Fracture Characterization and Fluid Flow, 1996*]. Especially the characterization of the transmissivity is very uncertain and difficult to obtain. Derivation based on cubic's law and a measured aperture distribution has been applied, but subsequent calibration is often required [*Finsterle, 2000*].

Another difficulty of the explicit fracture description is to determine which fractures effectively transport water. A large part of a fracture network might be nonconductive, and a model based on all visible fractures will thus overestimate the interconnectivity and thereby the overall fracture flow. Additionally, it has been found that channeling can take place in conductive fractures and only a small part of a fracture plane thereby contributes to the flow (see Section 1.5.1). To account for this channeling, models where the fracture domain is represented by a channel network have been developed [e.g., *Gylling et al., 1999; Cacas et al., 1990a; Cacas et al., 1990b*].

Discrete fracture network models that also include the matrix has been developed e.g. by *Sudicky and McLaren* [1992] for saturated conditions and by *Therrien and Sudicky* [1996] for unsaturated conditions. The difficulties in including the matrix is the different time scale involved for transport along the fractures and in the matrix and the need for a fine grid resolution to represent sharp concentration gradients at the fracture-matrix interface. By applying a Laplace transform Galerkin method in conjunction with a finite-element model, *Sudicky and McLaren* [1992] were able to solve the problem numerically. Fractures are represented by 1-D planes and the porous matrix is represented in 2-D; however, it can be numerically challenging if there are many fractures in the model [*Lee et al., 2001*]. The application of discrete fracture network models on unsaturated systems is additionally described in Section 1.8.4.

The main advantage of the discrete fracture network models is the ability to simulate small-scale processes. Compared to continuum models the volume-averaging approximations are avoided at the scale of the fracture network. Additionally, disconnected fractures can be simulated whereas the continuum models assume fracture systems that are regular and well connected. However, to be useful as a simulation tool, discrete network models must incorporate information concerning the dominating fracture features and their positions in 3-D space. The main disadvantages of the discrete network models are (1) the difficulties in obtaining the required statistical information, (2) the difficulties in separating the conductive fracture geometry from the nonconductive fracture geometry, and (3) the complexity of modeling realistic fracture densities [*National Research Council Committee on Fracture Characterization and Fluid Flow, 1996*]. Because of the complexity, the discrete fracture network models have had limited application in modeling

multiphase flow and transport in fractured media for large-scale problems and have generally only been used to study small-scale problems [*Wu, 2000; Lee et al., 2001*].

1.8.3 Hybrid models

Hybrid models (also known as mixed discrete-continuum models) have been proposed as a method for flow and transport modeling in fractured media that combines discrete fracture network models with the continuum approach. The discrete fracture network models can realistically describe the distribution of fractures and the interactions between fractures and matrix. However, because of its complexity it can only by applied to small-scale studies. The continuum approach is simple, but can easily miss local dominant phenomena. The approach of the hybrid model is to identify the dominant fractures and model them as 2-D features embedded in a 3-D porous medium that represents the remaining fractures. The concept thus shares the simplicity of continuum models while presumably capturing the role of the most important fractures [*Carrera and Martinez-Landa, 2000*]. An example of a hybrid model is presented by *Lee et al.* [2001], where the fractures are classified on the basis of their length compared to the finite difference grid size. The small fractures are modeled analytically and included as an enhancement of the permeability. This information is used in the second step, where the contribution of medium fractures to the effective permeability is modeled by a boundary element method and long fractures are modeled explicitly.

1.8.4 Modeling of unsaturated fractured porous media

Several of the presented approaches have also been applied for modeling flow and transport in unsaturated fractured systems. The same approaches are applied, but flow is described by Richards' equation and capillary functions are applied for both fractures and matrix. The most common models in variably saturated fractured media are the continuum concepts [*Pruess et al., 1999*]. Especially dual-permeability models that describe migration of water and solute in both fractures and matrix are common [e.g. *Gerke and van Genuchten 1993a; Ray et al., 1997; Vogel et al., 2000*]. The media is represented by two continua representing the fracture and matrix, respectively. For each continuum, flow is described by Richards' equation and solute transport by the advection-dispersion equation. Between the two continua, fluid and solute interactions are described by first-order mass-transfer functions. An example of a dual-permeability model is the 1-D model developed by *Gerke and van Genuchten* [1993a], which also have been extended to 2-D by *Vogel et al.* [2000]. The 1-D flow equations are given by the following two equations, where index f and m is representative for fracture and matrix, respectively [*Gerke and van Genuchten, 1993a*]:

$$C_f \frac{\partial h_f}{\partial t} = \frac{\partial}{\partial x}\left(K_f \frac{\partial h_f}{\partial x} - K_f \right) - \frac{\Gamma_w}{w_f} \tag{1.32}$$

$$C_m \frac{\partial h_m}{\partial t} = \frac{\partial}{\partial x}\left(K_m \frac{\partial h_m}{\partial x} - K_m \right) - \frac{\Gamma_w}{1 - w_f} \tag{1.33}$$

where w_f is the fracture volumetric fraction per unit volume of the bulk soil, and Γ_w is the coupling term, defined as the volume of fluid moving from the fracture to the matrix region per unit bulk volume of the media [1/s].

The coupling term describing the exchange of water between the two domains is assumed to be proportional to the difference in pressure between the matrix and the fracture regions. *Gerke and van Genuchten* [1993b] define the coupling term as:

$$\Gamma_w = \alpha_w (h_f - h_m) \tag{1.34}$$

$$\alpha_w = \frac{a}{l^2}\gamma K_a \tag{1.35}$$

where α_w is the coupling parameter [$1/m^2$], K_a is the unsaturated hydraulic conductivity at the interface [m/s], a is a geometry factor [-], γ_w is en empirical coefficient estimated to be 0.4, and l is the distance from the center of the matrix block to the fracture boundary [m].

Transport is also described by two advection dispersion equations where mass transfer between the two domains is allowed. The 1-D equations include sorption, but neglect degradation [*Gerke and van Genuchten, 1993a*]:

$$\frac{\partial}{\partial t}(\theta_f R_f c_f) = \frac{\partial}{\partial x}\left(\theta_f D_f \frac{\partial c_f}{\partial x} - q_f c_f\right) - \frac{\Gamma_s}{w_f} \tag{1.36}$$

$$\frac{\partial}{\partial t}(\theta_m R_m c_m) = \frac{\partial}{\partial x}\left(\theta_m D_m \frac{\partial c_m}{\partial x} - q_m c_m\right) + \frac{\Gamma_s}{1 - w_f} \tag{1.37}$$

where Γ_s is the exchange factor, defined as the mass of solutes per unit volume of bulk soil per unit time. Both advection and diffusion will contribute to Γ_s and the following equations are given by *Gerke and van Genuchten* [1993a]:

$$\Gamma_s = (1-d)\Gamma_w \phi_f c_f + d\Gamma_w \phi_m c_m + \alpha_s (1 - w_f)(c_f - c_m) \tag{1.38}$$

where

$$d = 0.5\left(1 - \frac{\Gamma_w}{|\Gamma_w|}\right) \tag{1.39}$$

$$\phi_f = w_f \frac{\theta_f}{\theta} \quad ; \quad \phi_m = (1 - w_f)\frac{\theta_m}{\theta} \tag{1.40}$$

where Γ_w is the exchange term for water as defined in Equation (1.34), d is a dimensionless coefficient determining the direction of the flow, ϕ_f and ϕ_m are dimensionless coefficient relating the solute concentration of the fracture and matrix to the unit solute mass of the bulk soil, and α_s is the solute transfer coefficient defined as in Equation 1.20. The first two terms in equation (1.38) defines the advective contribution to Γ_w and the last term is the diffusive contribution. The latter is equivalent to the mass transfer term given in the double-porosity model as presented in equation (1.17); the only difference is the product ($1-w_f$) which specifies the volume of water in the matrix pore system per unit bulk volume.

A very important parameter in the dual-permeability model is, Γ_w, describing the fracture-matrix fluid interaction. Several researchers have found that traditional dual-permeability models tend to overpredict the interactions between the two continua, since they assume that all the fractures flow with full fracture/matrix surface area [*Pruess, 1999*]. However, several mechanisms result in a nonuniform distribution of water in unsaturated fractures. As described in Section 1.5.2 fingering may take place under unsaturated conditions and furthermore are not all fractures likely to be connected and active. This will reduce the fracture-matrix interface area and thereby reduce the

interaction taking place. Additionally, coatings on the fracture walls can reduce the imbibition into the matrix, which is not incorporated into the traditional models. Various methods have been proposed to reduce the coupling term and thereby the fracture-matrix flux, such as the dependence on the fracture saturation or the liquid relative permeability [*Bandurraga et al., 1999*]. *Liu et al.* [1998] developed a method where the fraction of active fractures in a connected fracture network was described as a function of the effective water saturation in the connected fractures. This expression was incorporated into a new description of both capillary pressure and relative permeability relations for the fracture network and additionally into an expression for the fracture-matrix interface area reduction factor. The preferential flow known to exist in unsaturated fractures were thus incorporated into the dual-permeability approach at a fracture network scale [*Liu et al., 1998*].

Based on the nature of flow discovered in unsaturated fractures in recent years, several researchers have questioned the application of continuum models on unsaturated fractured systems. *Pruess et al.* [1999] conclude that macroscale continuum concepts may be inadequate to resolve the spatially localized and time-varying flow phenomena observed in unsaturated fractures, and thereby not include the fast preferential flow paths. The conventional volume-average approaches may thus provide unrealistic estimates of travel times when calculating transport of contaminants through vadose fractured rock. Another problem with the dual-permeability models is to obtain independent hydraulic properties for both the fracture and the matrix domains. Additionally, tweaking of the parameters are required to be able to sustain fracture flow in the presence of a partially saturated matrix and thereby obtain the fast preferential flow observed experimentally [*Pruess et al., 1999*]. Thus estimates of realistic parameters for dual-permeability models are difficult to obtain [*Ray et al., 1997; Pruess et al., 1999*].

Discrete fracture network models have also been developed for unsaturated fractured systems. FRAC3DVS by *Therrien and Sudicky* [1996] is a 3-D model describing variably saturated flow in a discrete fracture network that includes flow and transport in a variable saturated matrix. Flow in the matrix is described by Richards' equation, and relative permeability and saturation-pressure head relationships are given by the functional relations presented by *van Genuchten* [1980]. The fractures are presented explicitly as 2-D parallel plates and flow is described by a combination of the saturated fracture flow equation and Richards' equation. Relative permeability and saturation-pressure head relationships are also required to describe variably-saturated flow in the fractures, however, there are very few studies where these relationships have been derived experimentally. The discrete fracture network models also have to consider a reduction of the area available for flow across a fracture-matrix interface, like described above for the dual-permeability models. This is to assure that as a fracture desaturate some parts will not conduct water. As described in Section 1.8.2 the large amount of data required for a discrete fracture model is difficult to obtain. This limits the application of this type of model to small-scale systems or experiments where only a few fractures control the flow.

Alternative approaches for modeling unsaturated fractured systems have been proposed. These include among others percolation theory, chaos theory, and the more simple phenomenological models. A review of the different approaches is given by *Pruess et al.* [1999] and will not be described further here.

1.8.5 Modeling of colloid transport

Modeling of colloids differs from solute modeling because of the severe retardation of colloids as described in Section 1.6.2. A dual-porosity model that describes colloid transport in saturated fractured media is presented by *Carapcioglu and Wang* [1999]. The effect of residual air on colloid transport has been modeled in porous media by *Corapcioglu and Choi* [1996]. To the author's knowledge no modeling approaches describing colloid transport in unsaturated fractured media has been developed, and will thus not be described further in this report.

1.8.6 Application of dual-continua models

Dual-continua models are as described above the most common approach for modeling fractured systems because of their simplicity. The 1D dual-porosity model CXTFIT by *van Genuchten and Wierenga* [1976] was applied to the tracer experiments in fractured clayey till described in Section 1.7.4 and presented by *Mortensen et al.* [2001b]. The model is a mobile-immobile model with a first-order mass transfer between the two domains as described in Section 1.8.1. An inverse estimation of parameters was conducted for each single tracer breakthrough curve obtained in the experiments. Input parameters were: the average pore water velocity v (based on the flux and the matrix porosity), the block length L, the input concentration c_0, and the pulse time t_0. For each breakthrough curve, the following parameters were estimated: the dispersion coefficient D, the β-value, the Damkohler number ω, and for the fluorescent dye tracers also the retardation factor R.

The estimates of the fluorescent dye tracers were not successful and resulted in physically unrealistic values for both the Damkohler number ω and the retardation factor R. Likely, the problem was distinguishing between sorption and diffusion processes, however, independently measured values for the dye sorption was not available to investigate this hypothesis further. For the anions and fluorobenzoic acids the model was only able to fit the first advection-dominated part of the breakthrough curve, whereas the match for the diffusion-dominated tailing was less successful. However, at low intensity where a double peak breakthrough curve was obtained, the model matched both parts of the breakthrough curve fairly well. The estimated parameters were not all physically realistic. Dispersivity values >1 m were generally obtained and even one of the estimate showed a dispersivity >5 m. The high dispersivity values were, however, correlated with very high values of the mean square error, indicating a general poor estimate. Also high values for the β-value were obtained, which describe the fraction of mobile water, i.e. the fraction of water in the fracture. The values did generally decrease with the water intensity as expected, however high values of 14-18 % at high intensity and 9-10% at low intensity were obtained.

Hu and Brusseau [1995] also applied the CXTFIT model to estimate parameters in a column experiment with macropores. They found, that the estimated β-value, i.e. the fraction of water in the fractures, was much larger than assumed for the set-up. They concluded that the model failed to describe this type of set-up, likely because the system was composed of higher-flow and lower-flow domains, instead of advective and nonadvective domains.

Also *Haggerty et al.* [2001] found physically unreasonable estimates for porosity and dispersivities when applying a dual-porosity model to match tracer experiments in fractured dolomite. Only the first part of the curve could be estimated, roughly corresponding to the advection/dispersion-dominated part, whereas the model failed to estimate the diffusion-dominated tailing. Instead, a multi-rate dual-porosity model was applied to the system, where diffusion of mass between the

mobile and immobile domain is described by a range of diffusion rate coefficients, as presented in Section 1.8.1. By allowing for a distribution of rate coefficients, the diffusion-dominated part of the breakthrough curve was matched very well and better parameters were obtained. This improvement over the single-rate double-porosity model was thus achieved with one additional parameter.

As described earlier other processes may result in breakthrough tailing as well, but since these processes are not described by the model, it is likely that they contribute to the partial failure of the dual-porosity model. For saturated conditions, the channeling observed within the fracture planes creates stagnant water that also participates in the diffusive exchange. This increased diffusive exchange should, however, only result in higher estimates for mass transfer. At unsaturated conditions, complex flow patterns like fingering and film-flow will affect the diffusion of solutes into the matrix and other areas with stagnant water. This type of flow and transport is not represented by the models and may contribute to its partial failure. Additionally, the influence of Taylor dispersion on the transport is not included in the model. The model assumes a linear dependence of dispersion, which has been shown not always to be true for fractured media where Taylor dispersion are more dominant (see Section 1.6.1). This deviation may result in unrealistic model estimates for the dispersion. Furthermore, heterogeneity in the fracture plane may result in non-Fickian dispersion as described previously, and thereby also affect the estimated model parameters. Modeling of fracture flow and transport are thus not an easy task. The simple models seem to produce parameters that are not physically realistic, however, the more complex models require data that are often unavailable in large-scale field experiments.

1.9 Conclusions

Preferential flow was examined in different unsaturated porous media and at different scales. First the influence of preferential flow in small-scale drainage experiments in relative homogeneous sand was examined with the purpose of quantifying reasons for nonuniqueness in unsaturated hydraulic properties. Second, tracer experiments were conducted in highly fractured unsaturated clayey till to examine the influence of preferential flow and transport.

In the first part of the study, reasons for random and nonunique behavior observed in drainage experiments conducted to determine unsaturated hydraulic properties were examined. By applying the light transmission technique on a thin translucent sand sample, the drainage processes were visualized at different initial conditions and at different boundary steps. The drainage was found to be composed of a mixture of fast air fingering and slower air back-filling. The influence of each of these microscale processes was controlled by a combination of the size and the speed of the applied boundary step, small-scale heterogeneities, and the initial saturation and its structure. Especially, heterogeneity near the bottom boundary was found to influence the measured outflow at high boundary steps. As air fingers reached the porous plate at the bottom boundary they moved horizontally and practically closed for further drainage. This resulted in similar outflow for different high boundary steps and thereby a nonunique behavior. The initial saturation had as expected influence on the obtained outflow, however, the experiments also revealed that the structure of the initially entrapped air has influence on the amount of water draining. This finding explained the previously observed random behavior, where experiments with near identical initial saturation, but with expected differences in structure, gave different results. Different micro-scale processes are thus important for the effective macroscale behavior and thereby also the measurement of unsaturated hydraulic properties, which suggest limitations on the current definitions and uniqueness of unsaturated hydraulic properties.

In the second part of the study, preferential flow in unsaturated fractured clayey till was examined. Current monitoring and sampling techniques in fractured vadose zone often fail to characterize the fast preferential flow. To circumvent this problem experiments were conducted in an isolated block (3.5 m x 3.5 m x 3.3 m), which allowed for full control of the water balance and gave area-integrated breakthrough curves. Multiple tracing experiments showed the water intensity had large influence on the observed breakthrough curves. At high water intensities, the obtained tracer breakthrough showed a traditional asymmetrical behavior where a fast peak was followed by a long tailing period. At low intensity, two of the applied tracers revealed a double peak breakthrough curve, whereas the tracer with the lowest molecular diffusion only showed one peak. The differences were hypothesized to be caused by severe diffusion into stagnant areas by the tracers with the highest diffusion coefficients. This was supported by the breakthrough curves obtained from the colloidal tracer, which experienced earlier breakthrough and only one tracer peak. The mobile-immobile model CXTFIT was used to describe the results. The model fitted the data fairly well, however, the parameters obtained were non realistic. Different reasons were suggested for the discrepancies like fingering and film flow in the fractures, heterogeneous matrix diffusion, and non-Fickian dispersion.

1.10 References

Bandurraga, T. M., and G. S. Bodvarsson, Calibrating hydrological parameters for the 3-D site-scale unsaturated zone mode of Yucca Mountain, Nevada, *J. Contam. Hydrol., 38*, 25-46, 1999.

Becker, M. W., P. W. Reimus, and P. Vilks, Transport and attenuation of carboxylate-modified latex microspheres in fractured rock laboratory and field tracer tests, *Ground Water, 37*(3), 387-394, 1999.

Becker, M. W., and A. M. Shapiro, Tracer transport in fractured crystalline rock: Evidence of nondiffusive breakthrough tailing, *Water Resour. Res., 36*(7), 1677-1686, 2000.

Benson, C. F., and R. S. Bowman, Tri- and tetrafluorobenzoates as nonreactive tracers in soil and groundwater. *Soil Sci. Soc. Am. J., 58*, 1123-1129, 1994.

Birkholzer, J., and C. Tsang, Solute channeling in unsaturated heterogeneous porous media, *Water Resour. Res., 33*(10), 2221-2238, 1997.

Birkholzer, J., G. Li, C.-F. Tsang, and Y. W. Tsang, Modeling studies and analysis of seepage into drifts at Yucca Mountain, *J. Contam. Hydrol., 38*, 349-384, 1999.

Birkhölzer, J., H. Rubin, H. Daniels, and G. Rouvé, Contaminant advection and spreading in a fractured permeable formation: Part 2. Numerical simulation, *J. Hydrol., 144*, 35-58, 1993.

Bowman, R. S., and J. F. Gibbens, Difluorobenzoates as nonreactive tracers in soil and ground water, *Ground Water, 30*(1), 8-14, 1992.

Brown, S., A. Caprihan, and R. Hardy, Experimental observations of fluid flow channels in a single fracture, *J. Geophys. Res., 103*(B3), 5125-5132, 1998.

Brusseau, M. L., R. E. Jessup, and P.S.C. Rao, Modeling the transport of solutes influenced by multiprocess nonequilibrium, *Water Resour. Res., 25*(9), 1971-1988, 1989.

Brusseau, M. L., The influence of solute size, pore water velocity, and intraparticle porosity on solute dispersion and transport in soil, *Water Resour. Res., 29*(4), 1071-1080, 1993.

Cacas, M. C., E. Ledoux, G. de Marsily, B. Tillie, A. Barbreau, E. Durand, B. Feuga, and P. Peaudecerf, Modeling fracture flow with a stochastic discrete fracture network: Calibration and validation. 1. The flow model, *Water Resour. Res., 26*(3), 479-489, 1990a.

Cacas, M. C., E. Ledoux, G. de Marsily, A. Barbreau, P. Calmels, B. Gillard, and R. Margritta, Modeling fracture flow with a stochastic discrete fracture network: Calibration and validation. 2. The transport model, *Water Resour. Res., 26*(3), 491-500, 1990b.

Callahan, T. J., P. W. Reimus, R. S. Bowman, and M. J. Haga, Using multiple experimental methods to determine fracture/matrix interactions and dispersion of nonreactive solutes in saturated volcanic tuff, *Water Resour. Res., 36*(12), 3547-3558, 2000.

Carrera, J., X. Sánchez-Vila, I. Benet, A. Medina, G. Galarza, J. Guimerá, On matrix diffusion: formulations, solution methods and qualitative effects, *Hydrogeo. J., 6*, 178-190, 1998.

Carrera, J., and L. Marinez-Landa, Mixed discrete-continuum models: A summary of experiences in test interpretation and model prediction, in *Dynamics of Fluids in Fractured Rock*, edited by B. Faybishenko, P. A. Witherspoon, and S. M. Benson, pp. 251-265, Geophysical Monograph 122, American Geophysical Union, Washington DC, 2000.

Chrysikopoulos, C. V., and Y. Sim, One-dimensional virus transport in homogenous porous media with time dependent distribution coefficient, *J. Hydrol., 185*, 199-219, 1996.

Corapcioglu, M. Y., and H. C. Choi, Modeling colloid transport in unsaturated porous media and validation with laboratory column data, *Water Resour. Res., 32*(12), 3437-3449, 1996.

Corapcioglu, M. Y., and S. Wang, Dual-porosity groundwater contamination transport in the presence of colloids, *Water Resour. Res., 35*(11), 3261-3273, 1999.

Corey, A. T., *Mechanisms of Immiscible Fluids in Porous Media*, Water Resour. Publ., Highlands Ranch, Colo., 1985.

Cote, C. M., K. L. Bristow, and P. J. Ross, Increasing the efficiency of solute leaching: impacts of flow interruption with drainage of the "preferential" flow paths, *J. Contam. Hydrol., 43*, 191-209, 2000.

Cumbie, D. H., and L. D. McKay, Influence of diameter on particle transport in a fractured shale saprolite, *J. Contam. Hydrol., 37*(1-2), 139-157, 1999.

Dahan, O., R. Nativ, E. Ador, B. Berkowitz and Z. Ronen, Field observation of flow in a fracture intersecting unsaturated chalk, *Water Resour. Res., 35*(11), 3315-3326, 1999.

Dahan, O., R. Nativ, E. M. Ador, B. Berkowitz, and N. Weisbrod, On fracture structure and preferential flow in unsaturated chalk, *Ground Water, 38*(3), 444-451, 2000.

Davis, S. N., D. J. Campbell, H. W. Bentley and T. J. Flynn, *Ground Water Tracers*, National Water Well Association, Worthington, Ohio, 1985.

de Marsily, G., *Quantitative Hydrogeology*. Groundwater Hydrology for Engineers, Academic Press, Inc., London, 1986.

Detwiler, R. L., H. Rajaram, and R. J. Glass, Solute transport in variable-fractures: An investigation of the relative importance of Taylor dispersion and macrodispersion, *Water Resour. Res., 36*(7), 1611-1625, 2000.

Doughty, C., Investigation of conceptual and numerical approaches for evaluating moisture, gas, chemical, and heat transport in fractured unsaturated rock, *J. Contam. Hydr., 38*, 69-106, 1999.

Doughty, C., Numerical model of water flow in a fractured basalt vadose zone: Box Canyon site, Idaho, *Water Resour. Res., 36*(12), 3521-3524, 2000.

Dullien, F. A. L., *Porous Media, Fluid Transport and Pore Structure*, Academic Press, Calif., 1992.

Eching, S. O., J. W. Hopmans, and O. Wendroth, Unsaturated hydraulic conductivity from transient multi-step outflow and soil water pressure data, *Soil. Sci., Soc. Am. J., 58*, 678-695.

Faybishenko, B., C. Doughty, M. Steiger, J. C. S. Long, T. R. Wood, J. S. Jacobsen, J. Lore, and P. T. Zawislanski, Conceptual model of the geometry and physics of water flow in a fractured basalt vadose zone, *Water Resour. Res., 36*(12), 3499-3520, 2000.

Finsterle, S., Using the continuum approach to model unsaturated flow in fractured rock, *Water Resour. Res., 36*(8), 2055-2066, 2000.

Forrer, I., A. Papritz, R. Kasteel, H. Flühler, and D. Luca, Quantifying dye tracers in soil profiles by image processing, *Europ. J. Soil Science, 51*, 313-322, 2000.

Gelhar, L.W., C. Welty, and K. R. Rehfeldt, A critical review of data on field-scale dispersion in aquifers, *Water Resour. Res., 28*(7), 1955-1974, 1992.

Gerke, H.H. and M. Th. van Genuchten, A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media, *Water Resour. Res., 29*(2), 305-319, 1993a.

Gerke, H.H. and M. Th. van Genuchten, Evaluation of a first-order water transfer term for variably saturated dual-porosity flow models, *Water Resour. Res., 29*(4), 1225-1238, 1993b.

Glass, R. J., and M. J. Nicholl, Physics of gravity fingering in immiscible fluids within porous media: An overview of current understanding and selected complicating factors, *Geoderma, 70*, 133-163, 1996.

Glass, R. J. and L. Yarrington, Simulation of gravity fingering in porous media using a modified invasion percolation model, *Geoderma, 70*, 231-252, 1996.

Gylling, B., L. Moreno, and I. Neretnieks, The channel network model – A tool for transport simulations in fractured media, *Ground Water, 37*(3), 367-375, 1999.

Hadermann, J., and W. Heer, The Grimsel (Switzerland) migration experiment: integrating field experiments, laboratory investigations and modeling, *J. Contam. Hydrol., 21*, 81-100, 1996.

Haggerty, R., and S. M. Gorelick, Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity, *Water Resour. Res., 31*(10), 2383-2400, 1995.

Haggerty, R., S. W. Fleming, L. C. Meigs, and S. A. McKenna, Tracer tests in a fractured dolomite 2. Analysis of mass transfer in single-well injection-withdrawel tests, *Water Resour. Res., 37*(5), 1129-1142, 2001.

Hassanizadeh, S.M., On the transient non-Fickian dispersion theory, *Trans. Por. Media, 23*, 107-124, 1996.

Hinsby, K., L. D. McKay, P. Jørgensen, M. Lenczewski, and C. P. Gerba, Fracture aperture measurements and migration of solutes, viruses, and immiscible creosote in a column of clay-rich till, *Ground Water, 34*(6), 1065-1075, 1996.

Hollenbeck, K. J., and K. H. Jensen, Experimental evidence of randomness and nonuniqueness in unsaturated outflow experiments designed for hydraulic parameter estimation, *Water Resour. Res., 34*(4), 595-602, 1998.

Hopmans, J. W., T. Vogel, and P. D. Koblik, X-ray tomography of soil water distribution in one-step outflow experiments, *Soil Sci. Soc. Am. J., 56*, 355-362, 1992.

Hopmans, J. W., and J. Ŝimůnek, Review of inverse estimation of soil hydraulic properties, in *Proceedings of the International Workshop on Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, edited by M. Th. van Genuchten, F. J. Leij, and L. Wu, pp. 643-659, U.S. Salinity Lab., Riverside, Calif., 1999.

Hu, Q., and M. L. Brusseau, Effect of solute size on transport in structured porous media, *Water Resour. Res., 31*(7), 1637-1646, 1995.

Jardine, P. M., W. E. Sanford, J. P. Gwo, O. C. Reedy, D. S. Hicks, J. S. Riggs, and W. B. Bailey, Quantifying diffusive mass transfer in fractured shale bedrock, *Water Resour. Res., 35*(7), 2015-2030, 1999.

Jardine, P. M., S. C. Brooks, G. V. Wilson, and W. E. Sanford, Basic research strategies for resolving remediation needs in contaminated fractured media, in *Dynamics of Fluids in Fractured Rock*, edited by B. Faybishenko, P. A. Witherspoon, and S. M. Benson, pp. 389-400, Geophysical Monograph 122, American Geophysical Union, Washington DC, 2000.

Kasnavia, T., D. Vu, and D. A. Sabatini, Fluorescent dye and media properties affecting sorption and tracer selection, *Ground Water, 37*(3), 376-381, 1999.

Kasteel, R., I. Forrer, H. Flühler, and K. Roth, Solute transport estimated by field- and laboratory-determined hydraulic parameters, in *Proceedings of the International Workshop on Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media*, edited by M. Th. van Genuchten, F. J. Leij, and L. Wu, pp. 1485-1495, U.S. Salinity Lab., Riverside, Calif., 1999.

Klint, K. E. S., and P. Gravesen,. Fractures and biopores in weichselian clayey till aquitards at Flakkebjerg, Denmark, *Nordic Hydrol., 30*(4/5), 267-284, 1999.

Klute, A. (Ed.), *Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods*, 2nd ed., in *Agronomy*, vol. 9, Am. Soc. of Agron., Soil Sci. Soc. of Am., Madison, Wisc., 1986.

Knapp, R. B., M. L. Chiarappa, and W. B. Durham, An experimental exploration of the transport and capture of abiotic colloids in a single fracture, *Water Resour. Res., 36*(11), 3139-3149, 2000.

Kool, J. B., J.C. Parker, and M. Th. van Genuchten, Determining soil hydraulic properties from one-step outflow experiments by parameter estimation. I. Theory and numerical studies, *Soil Sci. Soc. Am. J., 49*, 1348-1354, 1985.

Kueper, B. H., and E. O. Frind, An overview of immiscible fingering in porous media, *J. Contam. Hydrol., 2*, 95-110, 1988.

Käss, W., *Tracing Technique in Geohydrology*, A.A. Balkema/Rotterdamm/Brookfield, 1998.

Lee, S. H., M. F. Lough, and C. L. Jensen, Hierarchical modeling of flow in naturally formations with multiple length scales, *Water Resour. Res., 37*(3), 443-455, 2001.

Lenormand, R., E. Touboul, and C. Zarcone, Numerical models and experiments on immiscible displacements in porous media, *J. Fluid. Mech., 189*, 165-187, 1988.

Lenormand, R., Liquids in porous media, *J. Phys: Condens. Matter 2*, sa79-sa88, 1990.

Liu, H. H., C. Doughty, and G. S. Bodvarsson, An active fracture model for unsaturated flow and transport in fractured rocks, *Water Resour. Res., 34*(10), 2633-2646, 1998.

Long, J. C. S., J. S. Remer, C. R. Wilson, and P. A. Witherspoon, Porous media equivalents for networks of discontinuous fractures, *Water Resour. Res., 18*(3), 645-658, 1982.

Maloszewski, P., A. Herrmann, and A. Zuber, Interpretation of tracer tests performed in fractured rock of the Lange Bramke basin, Germany, *Hydrogeo. J., 7*, 209-218, 1999.

Manz, B, P. Alexander, and L. F. Gladden, Correlations between dispersion and structure in porous media probed by nuclear magnetic resonance, *Physics of Fluids, 2(11)*, 259-267, 1999.

McCarthy, J. F., K. M. Howard, and L. D. McKay, Effect of pH on sorption and transport of fluorobenzoic acid groundwater tracers, *J. Environ. Qual., 29*, 1806-1813, 2000.

McKay, L. D., R. W. Gillham, and J. A. Cherry, Field experiments in a fractured clay till 2. Solute and colloid transport, *Water Resour. Res., 29*(12), 3879-3890, 1993.

McKay, L. D., P. L. Stafford, and L. E. Toran, EPM modeling of a field-scale tritium tracer experiment in fractured, weathered shale, *Ground Water, 35*(6), 997-1007, 1997.

McKay, L. D., W. E. Sanford, and J. M. Strong, Field-scale migration of colloidal tracers in a fractured shale saprolite, *Ground Water, 38*(1), 139.147, 2000.

Meigs, L. C., and R. L. Beauheim, Tracer tests in a fractured dolomite 1. Experimental design and observed tracer recoveries, *Water Resour. Res., 37*(5), 1113-1128, 2001.

Moreno, L., and C. F. Tsang, Multiple peak response to tracer injection tests in single fractures: A numerical study, *Water Resour. Res., 27*(8), 2143-2150, 1991.

Mortensen, A. P., R. J. Glass, K. Hollenbeck, and K. H. Jensen, Visualization of microscale phase displacement processes in retention and outflow experiments: Nonuniqueness of unsaturated flow properties, *Water Resour. Res., 37*(6), 1627-1640, 2001a.

Mortensen, A. P., K. H. Jensen, B. Nielsson, and R. K. Juhler, Multiple tracing experiments in unsaturated fractured clayey till, *This report, Part 3*, 2001b.

National Research Council Committee on Fracture Characterization and Fluid Flow, *Rock Fractures and Fluid Flow: Contemporary Understanding and Applications*, Natl. Acad. Press, Washington D. C., 1996.

Nicholl, M. J., R. J. Glass, and S. W. Wheatcraft, Gravity-driven infiltration instability in initially dry nonhorizontal fractures, *Water Resour. Res., 30*(9), 2533-2546, 1994.

Nkedi-Kizza, P., J. W. Biggar, H. M. Selim, M. Th. van Genuchten, P. J. Wierenga, J. M. Davidson and D. R. Nielsen, On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol, *Water Resour. Res., 20*(8), 1123-1130, 1984.

Parker, J. C., and A. J. Valocchi, Constraints on the validity of equilibrium and first-order kinetic transport models in structured soils, *Water Resour. Res., 22*(3), 399-407, 1986.

Persoff, P., and K. Pruess, Two-phase flow visualization and relative permeability measurement in natural rough-walled rock fractures, *Water Resour. Res., 31*(5), 1175-1186, 1995.

Pruess, K., and T. N. Narasimhan, A practical method for modeling fluid and heat flow in fractured porous media, *Soc. Pet. Eng. J., 25*, 14-26, 1985.

Pruess, K., and Y. W. Tsang, On two-phase relative permeability and capillary pressure of rough-walled fractures. *Water Resour. Res., 26*(9), 1915-1926, 1990.

Pruess, K., B. Faybishenko, and G. S. Bodvarsson, Alternative concepts and approaches for modeling flow and transport in the thick unsaturated zones of fractured rocks, *J. Contam. Hydrol., 38*, 281-322, 1999.

Pruess, K., Multiphase flow in fractured rocks – some lessons learned from mathematical models, in *Dynamics of Fluids in Fractured Rock*, edited by B. Faybishenko, P. A. Witherspoon, and S. M. Benson, pp. 225-234, Geophysical Monograph 122, American Geophysical Union, Washington DC, 2000.

Ray, C., T. R. Ellsworth, A. J. Valocchi, and C. W. Boast, An improved dual porosity model for chemical transport in macroporous soils, *J. Hydrol., 193*, 270-292, 1997.

Reedy, O. C., P. M. Jardine, G. V. Wilson, and H. M. Selim, Quantifying the diffusive mass transfer of nonreactive solutes in columns of fractured saprolite using flow interruption, *Soil Sci. Soc. Am. J., 60*, 1376-1384, 1996.

Roux, S., F. Plouraboue, and J. P. Hulin, Tracer dispersion in rough open cracks, *Transp. Porous Media, 32*, 97-116, 1998.

Sabatini, D. A. and T. A. Austin, Characteristics of Rhodamine WT and fluorescein as adsorbing ground-water tracers, *Ground Water, 29*(3), 341-349, 1991.

Schoen, R., J. P. Gaudet, and T. Bariac, Preferential flow and solute transport in a large lysimeter, under controlled boundary conditions, *J. Hydrol., 215*, 70-81, 1999.

Stadler, D., M. Stähli, P. Aeby, and H. Flühler, Dye tracing and image analysis for quantifying water infiltration into frozen soils, *Soil Sci. Soc. Am. J., 64*, 505-516, 2000.

Stolte, J., J. I. Freijer, W. Bouten, C. Birksen, J. M. Halbertsma, J. C. van Dam, J. A. van den berg, G. J. Veerman, and J. H. M. Wösten, Comparison of six methods to determine unsaturated soil hydraulic conductivity, *Soil Sci. Soc. Am. J., 58*, 1596-1603, 1994.

Su, G. W., J. T. Geller, K. Preuss, and F. Wen, Experimental studies of water seepage and intermittent flow in unsaturated, rough-walled fractures, *Water Resour. Res., 35*(4), 1019-1037, 1999.

Su, G. W., J. T. Geller, K. Pruess, and J. Hunt, Overview of preferential flow in unsaturated fractures, in *Dynamics of Fluids in Fractured Rock*, edited by B. Faybishenko, P. A. Witherspoon, and S. M. Benson, pp. 147-155, Geophysical Monograph 122, American Geophysical Union, Washington DC, 2000.

Sudicky, E. A., and R. G. McLaren, The Laplace transform Galerkin technique for large-scale simulation of mass transport in discretely fractures porous formations, *Water Resour. Res., 28*(2), 499-514, 1992.

Therrien, R., and E.A. Sudicky, Three-dimensional analysis of variably-saturated flow and solute transport in discretely-fractured porous media. *J. Contam. Hydrol., 23*, 1-44, 1996.

Tidwell, V. C., and R. J. Glass, X-ray and visible light transmission for laboratory measurement of two-dimensional saturation fields in thin-lab systems, *Water Resour. Res., 30*(11), 2873-2882, 1994.

Tidwell, V. C, L. C. Meigs, T. Chritian-Frear, and C. M. Boney, Effects of spatially heterogeneous porosity on matrix diffusion as investigated by X-ray absorption imaging, *J. Contam. Hydrol., 42*, 285-302, 2000.

Tokunaga, T. K., and J. Wan, Water film flow along fracture surfaces of porous rock, *Water Resour. Res., 33*(6), 1287-1295, 1997.

Tokunaga, T. K., J. Wan, and S. R. Sutton, Transient film flow on rough fracture surfaces, *Water Resour. Res., 36*(7), 1737-1746, 2000.

Toride, N., F. J. Leij, and M. Th. van Genuchten, The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.1, *Research Report No. 137*, U.S. Salinity Laboratory Agricultural Research Service, U.S. Department of Agriculture, Riverside, California, 1995.

Tsang, Y. W., Usage of "equivalent apertures" for rock fractures as derived from hydraulic and tracer tests, *Water Resour. Res., 28*(5), 1451-1455, 1992.

Tsang, Y. W., Study of alternative tracer tests in characterizing transport in fractured rocks, *Geophys. Res. Letters, 22*(11), 1421-1424, 1995.

Ullum, M., *Effects of water content and soil structure on colloid transport in porous media*, Dept. of Hydrodynamics and Water Resources, Technical University of Denmark, 2000.

van Dam, J. C., J. N. M. Stricker, and P. Droogers, Inverse method for determining soil hydraulic functions from one-step outflow experiments, *Soil Sci. Soc. Am. J., 56*, 1042-1050, 1992.

van Dam, J. C., J. N. M. Stricker, and P. Droogers, Inverse method to determine soil hydraulic functions from multi-step outflow experiments, *Soil Sci. Soc. Am. J., 58*, 647-652, 1994.

van Genuchten, M. Th. and P. J. Wierenga, Mass transfer studies in sorbing porous media, 1, Analytical solutions, *Soil Sci. Soc. Am. J., 40*, 473-480, 1976.

van Genuchten, M. Th., A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Sci. Soc. Am. J., 44*, 892-898, 1980.

van Genuchten, M.Th. and R.J. Wagenet, Two-site/two region models for pesticide transport and degradation: Theoretical development and analytical solutions, *Soil Sci. Soc. Am. J., 53*(5), 1303-1310, 1989.

Villholth, K. G., N. J. Jarvis, O. H. Jacobsen, and H. de Jonge, Field investigations and modeling of particle-facilitated pesticide transport in macroporous soil, *J. Environ. Qual., 29*, 1298-1309, 2000.

Vink, J. P. M., B. Gottesbüren, B. Diekkrüger, S. E .A. T. M. van der Zee, Simulation and model comparison of unsaturated movement of pesticides from a large clay lysimeter, *Ecological Modeling, 105*, 113-127, 1997.

Vogel, T., H. H. Gerke, R. Zhang, and M. Th. van Genuchten, Modeling flow and transport in a two-dimensional dual-permeability system with spatially variable hydraulic properties. *J. Hydrol., 238*, 78-89, 2000.

Wan, J., and T. K. Tokunaga, Film straining of colloids in unsaturated media: conceptual model and experimental testing, *Environ. Sci. Technol., 31*, 2413-2420, 1997.

Wan, J., and J. L. Wilson, Visualization of the role of the gas-water interface on the fate and transport of colloids in porous media, *Water Resour. Res., 30*(1), 11-23, 1994.

Wang, J. S. Y, and T. N. Narasimhan, Hydrologic mechanisms governing fluid flow in a partially saturated, fractured, porous medium, *Water Resour. Res., 21*(12), 1861-1874, 1985.

Warren, J. E., and P. J. Root, The behavior of naturally fractured reservoirs, *Soc. Pet. Eng. J., 3*, 245-255, 1963.

Wildenschild, D., K. H. Jensen, K. Villholth, and T. H. Illangasekare, A laboratory analysis of the effect of macropores on solute transport, *Ground Water, 32*(3), 381-389, 1994.

Wildenschild, D., K. H. Jensen, K. J Hollenbeck, T. H. Illangasekare, D. Znidarcic, T. Sonnenborg, and M. B. Butts, A two-stage procedure for determining unsaturated hydraulic characteristics using a syringe pump and outflow observations, *Soil Sci. Soc. Am. J., 6*1(2), 347-359, 1997.

Wildenschild, D., J. W. Hopmans, and J. Simunek, Flow rate dependence of soil hydraulic characteristics, *Soil Sci. Soc. Am. J., 65*, 35-48, 2001.

Wilkinson, D., Percolation model of immiscible displacement in the presence of buoyancy forces. Physical Review A, Vol. 30, No. 1, pp. 520-531, 1984.

Witherspoon, P. A., J. S. Y. Wang, K. Iwai, and J. E. Gale, Validity of cubic law for fluid flow in a deformable rock fracture. *Water Resour. Res., 16*(6), 1016-1024, 1980.

Wu, Y-S., On the effective method for modeling multiphase flow, multicomponent transport, and heat transfer in fractured rock, in *Dynamics of Fluids in Fractured Rock*, edited by B. Faybishenko, P. A. Witherspoon, and S. M. Benson, pp. 299-312, Geophysical Monograph 122, American Geophysical Union, Washington DC, 2000.

Zimmerman, R. W., and I.-W. Yeo, Fluid flow in rock fractures: from the Navier-Stokes equations to the cubic law, in *Dynamics of Fluids in Fractured Rock*, edited by B. Faybishenko, P. A. Witherspoon, and S. M. Benson, pp. 213-224, Geophysical Monograph 122, American Geophysical Union, Washington DC, 2000.