Contaminant transport and attenuation in fissured argillites — a case study

J. MAIER & G. DÖRHÖFER
Geological Survey of Lower Saxony, Stilleweg 2, D-3000 Hannover, Germany

Abstract Based on a comprehensive field study conducted at the Münchehagen waste disposal site, the groundwater flow and solute transport characteristics of fissured argillites rocks are described. Particularly recent multi-tracer experiments and supplementary laboratory diffusion and batch sorption experiments are presented. The fissured rock behaves as an anisotropic homogeneous continuum with respect to permeability and storativity. Solute transport is strongly influenced by matrix diffusion and sorption. The preliminary results indicate that simple relationships between systems of parallel fractures and homogeneous aquifers can be used to roughly estimate solute transport characteristics of the fissured rocks.

INTRODUCTION

The groundwater flow and solute transport characteristics of fissured Lower Cretaceous (Valanginian) argillites are being investigated at the abandoned Münchehagen hazardous waste disposal site in Lower Saxony in order to assess and predict the development of the leachate plume and to evaluate the proposed remedial measures. In addition, the Münchehagen site is part of an extensive outcrop of Lower Cretaceous argillaceous rocks in Lower Saxony which has become an area of special interest for the siting of new landfills and special waste disposal facilities. Investigation and assessment of the geology beneath waste disposal sites is essentially focussed on the properties that characterize the rocks as a natural migration barrier. It is necessary to elucidate the relevant processes and key parameters in terms of their physical significance and to select (and if necessary modify) the most suitable and effective methods for their quantification.

So far, a comprehensive hydrogeological reconnaissance program has been carried out which includes a wide range of geoscientific field methods such as surface and borehole geophysical surveys, hydraulic testing, fracture mapping, groundwater sampling and hydraulic head monitoring (for more detail, see Gronemeier et al. (1990), Dörhöfer & Fritz (1991)). Further investigations are being concentrated on field and supplementary laboratory studies, i.e. field multi-tracer experiments and laboratory diffusion and batch-type experiments, to examine the aqueous phase transport of dissolved species (with special reference to organic contaminants) through fissured rocks and the dominant mechanisms of contaminant attenuation.

Site description

The Münchehagen waste disposal site is situated about 5 km southwest of the village of Münchehagen and about 40 km west of Hannover, Lower Saxony. It
lies in an area whose landscape and geology belong to the northern foreland of the German Mittelgebirge. The dominant regional structure is the Lower Saxony basin, which is characterized here by small-scale graben tectonics associated with E-W faults. Thick Lower Cretaceous mudstones are covered with thin Quaternary deposits, which are locally absent. Composition and physical properties of the Lower Cretaceous argillaceous rocks are summarized in Table 1.

<table>
<thead>
<tr>
<th>Grain size (%)</th>
<th>Total carbonate (%)</th>
<th>0 - 24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay (&lt; 2 µm)</td>
<td>32 - 59</td>
<td></td>
</tr>
<tr>
<td>Silt (2 - 63 µm)</td>
<td>43 - 64</td>
<td></td>
</tr>
<tr>
<td>Sand (&gt; 63 µm)</td>
<td>0 - 4</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Composition and physical properties (range of values) of the Lower Cretaceous (Valanginian) rock sequence at the Münchhagen site.

<table>
<thead>
<tr>
<th>Mineralogy (XRD) (%)</th>
<th>Spec.surface (BET) (m² g⁻¹)</th>
<th>Porosity (%)</th>
<th>Rock permeability (m s⁻¹)</th>
<th>6x10⁻¹¹ - 2x10⁻⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>15 - 51</td>
<td>2.0 - 2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite/Illite</td>
<td>20 - 41</td>
<td>5 - 24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite/Chlorite</td>
<td>21 - 40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>0 - 19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ankerite/Dolomite/Siderite</td>
<td>0 - 8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>0 - 6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Münchhagen waste disposal site consists of several basins, which differ with respect to size, period of operation, depth, and type of waste. Between 1968 and 1983 a wide variety of chemical residues and industrial bulk wastes, in total about 400 000 m³, were disposed of in 6 and 25 m deep open pits without any kind of technical barriers. Little prior study was carried out to determine the suitability of the site to receive hazardous wastes. Most of the waste lies below the shallow water table. The contamination of groundwater and soil by toxic organic chemicals (particularly persistent chlorinated aliphatic hydrocarbons, aromatic hydrocarbons, and chlorinated dibenzodioxins) has become a potential environmental hazard.

Monitoring of the observation well network has verified a down-gradient spread of a leachate plume (Fig. 1). Nonuniform disposal has resulted in a laterally and vertically differentiated migration pattern of various leachate compounds. Groundwater contamination by organic compounds is restricted to a narrow zone at the down-gradient margin of the disposal site. The aqueous phase concentrations fall by several orders of magnitude within a distance of less than 40 m to values approaching the local background or detection limit (Fig. 2). This provides evidence of highly effective attenuation mechanisms, which are assumed to be essentially matrix diffusion and sorption.

AQUIFER AND GROUNDWATER FLOW CHARACTERISTICS

The argillaceous rocks beneath the thin cover of unconsolidated clayey deposits (tillite and weathered Lower Cretaceous rocks) are strongly jointed. Analysis of fracture data indicates the existence of four distinct fracture sets, forming an
interconnected network of (planar) pathways for groundwater flow. The fracture spacing within the individual fracture sets is of the order of few tens of centimetres. The permeability of the rock is almost exclusively a function of the void space of the open fractures. The permeability of the rock matrix is 3-4 orders of magnitude smaller (about $k_f = 10^{-10} - 10^{-9} \text{ m s}^{-1}$) and does not contribute substantially to fluid flow. The equivalent effective fracture aperture

Fig. 1 Map of the Münchehagen waste disposal site.

Fig. 2 Aqueous-phase concentrations (maximum values) of sulphate and toluene starting from the waste deposit and decreasing with distance in direction of groundwater flow. Note different units of concentration.
(w) and equivalent fracture porosity \((n_f)\) can be calculated assuming an ideal parallel plate representation of the fractured medium (sets of continuous, smooth, parallel fractures of equal spacing \((d)\) and width), and using the relationship:

\[
k_f = \frac{\rho g w^3}{\nu 12d} \quad \text{and} \quad n_f = \frac{w}{d}
\]

where \(\rho, g,\) and \(\nu\) are the fluid density, the gravity acceleration constant and the fluid viscosity, respectively. Permeability and fracture spacing being in the range of \(k_f = 10^{-7} - 10^{-5} \text{ m s}^{-1}\) and \(d = 0.1 - 1 \text{ m}\) result in values of fracture aperture and porosity of \(w = 20 - 190 \mu\text{m}\) and \(n_e = 0.01 - 0.09\%\), respectively.

The permeability data have been obtained from extensive hydraulic testing (a total of about 350 straddle-packer tests in uncased borehole sections and several pumping tests in completed wells). The permeability tends towards a log-normal distribution. There is a general trend of decreasing permeability as well as decreasing number of fractures with depth, allowing a vertical subdivision of the aquifer with respect to permeability: a near-surface zone down to about 15 m below surface, a zone from about 15-40 m, and a zone deeper than 40 m below surface, having (geometric) mean permeabilities of \(1 \times 10^{-5}\), \(2 \times 10^{-6}\), and \(5 \times 10^{-7} \text{ m s}^{-1}\), respectively. This depth zonation of permeability is reflected in a depth zonation of groundwater composition. The spread of the contaminant plume takes place predominantly in the near-surface zone, which has a distinctly higher permeability than the deeper rock.

The hydrogeological investigations indicate that the fractured rock behaves as a more or less anisotropic, but statistically homogeneous continuum with respect to permeability and storativity. For most practical geohydrological considerations it can be treated as a porous medium using the conventional evaluation methods. Locally a pronounced anisotropy of hydraulic properties due to an E-W trending fault occurs (see Fig. 3, taking a pumping test carried out at the tracer test site as an example).

\[
T = \frac{a}{b} = \frac{T_x}{T_y}
\]

\[
T = \sqrt{T_x T_y}
\]

**Fig. 3** Direction-dependent transmissivity from a pumping test at the tracer test site due to hydraulic anisotropy. Calculation according to Hantush & Thomas (1966).
TRACER EXPERIMENTS

In order to evaluate the solute transport characteristics of the fractured rock mass, additional data is required. The particularly critical parameters, the effective fracture aperture and porosity cannot be determined directly. In addition, hydrodispersive transport in a fractured rock with a porous matrix depends considerably on the process known as matrix diffusion (Grisak & Pickens, 1980; Neretnieks, 1980), i.e. diffusion of dissolved substances out of the mobile water in the fractures into the more or less stagnant water occupying the pore space of the rock itself (and vice versa).

A test area was delineated in the Münchehagen site and groundwater tracer tests were carried out between August 1991 and December 1992 (Fig. 4). In all experiments, tracers were injected into a steady-state radial-convergent flow field established by pumping at a constant rate of 0.3 m$^3$ hour$^{-1}$. The forced hydraulic gradients were up to 50 times higher than the hydraulic gradients under natural flow conditions (natural $\Delta H = 0.005$). Samples were collected from the withdrawal well (vertically averaged). The breakthrough curves were plotted and normalized with respect to peak concentration $C_{\text{max}}$ or initial concentration $C_0$ ($C_0 = M (h \pi r_L^2)^{-1}$, where $M$ is the mass of tracer injected, $h$ is the length of the well screen, $r_L$ is the distance between input and withdrawal well in a radial-convergent flow field). In tracer test II, a conservative tracer (nitrate) and a suspension of polystyrene microparticles (2 μm diameter) were injected simultaneously. From direct comparison of the breakthrough curves, the influence of matrix diffusion can be demonstrated (Fig. 5). Most of the microparticles are sieved out or sedimented during transport in the groundwater. The remaining suspended particles however are not subject to any further attenuation mechanisms, in contrast to dissolved nitrate, which is subject to retardation by matrix diffusion. Thus, we see the particles travelling considerably faster than nitrate. The mean transit time of the microparticles provides the

![Fig. 4 Map of the tracer test site and overview of the tracer tests conducted. Arrows indicate the direction of flow between input and withdrawal well. Well spacing is 6 m. All wells have screens from 5-25 m below surface.](image-url)
interstitial velocity \( (v_a) \) of groundwater flow under the prevailing experimental conditions. Together with the measured permeability \( (k_f) \) and the hydraulic head difference \( \Delta H \) the effective porosity \( (n_e) \), referring to an equivalent porous medium) can be estimated using the expression \( v_a = k_f \Delta H n_e^{-1} \), where \( n_e = 0.09\% \).

The experimental setup for the tracer tests was oriented to correspond to the local permeability anisotropy previously determined. Tracer tests II and III were conducted approximately parallel to the direction of the predominant fracture set, i.e. the direction of the highest permeability, and tracer test I almost perpendicular to it. The impact of the test orientation on the tracer transport under otherwise identical experimental conditions is depicted in Fig. 6. Nitrate (tracer test II) as well as bromide (tracer test I) can be treated as conservative tracers and thus compared with each other. The difference between the tracer breakthroughs was greater than could be expected merely from the difference in permeability in the two directions at right angles. The fast propagation of nitrate is due to advection being the predominant transport mechanism in the direction of higher permeability. In contrast, solute transport in the direction of lower permeability is controlled by the comparatively slow process of matrix diffusion, i.e. with increasing transit time, more tracer is removed by diffusion from the fractures into the rock itself. This results in a considerable retardation, increased apparent dispersion and a pronounced "tailing" of the tracer breakthrough curve.

The ratio of the Darcy velocity to the actual interstitial velocity obtained from the bromide breakthrough curve gives a value for the equivalent effective

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**Fig. 5** Nitrate and microparticle breakthrough (tracer test I). Logarithmic time scale.

**Fig. 6** Nitrate (Tracer test I) and bromide (tracer test II) breakthrough. Dependence of tracer breakthrough on direction. Recovery (%) in brackets. Logarithmic time scale.
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This is approximately $n_e = 11\%$ and thus is of the same magnitude as the total porosity of the rock (fracture porosity $n_f$ plus rock-matrix porosity $n_m$). This means that for solute transport controlled by matrix diffusion, the tracer propagates as if spreading occurs through the total pore volume of the rock. This is consistent with theoretical considerations by Maloszewski & Zuber (1989) and Vogel & Giesel (1989) based on the analytical solution of transport in a system of ideal parallel fractures (Sudicky & Frind, 1982). They showed that for "long term tracer experiments" (meaning that diffusive equilibrium between matrix and fractures was established), retardation ($R$) of a solute with respect to bulk water movement due to matrix diffusion and sorption can be estimated using the ratio of matrix to fracture porosity:

$$ R \approx 1 + \frac{n_m}{n_f} $$

for a non-reactive solute, and

$$ R = 1 + \frac{n_m}{n_f} R_s $$

for a reactive solute, where $R_s$ is the retardation factor due to sorption in the rock matrix.

Figure 7 depicts the breakthrough curves of the slightly sorbing tracers (fluorescein and lithium) in comparison with non-reactive bromide. Even slight sorption tends to cause considerable retardation and apparent dispersion of the solute due to the interaction of the matrix diffusion and sorption processes. The bromide was nearly all retrieved (about 90%) after 7 months duration of the test, whereas mass recovery of fluorescein and lithium was only 45% and 20% respectively by the end of the test. The mass of solute that diffuses into and is sorbed by the rock matrix requires a long period of time to be released again. The significance of matrix diffusion with respect to transport of reactive solutes is that the very much larger specific surface of the rock itself is accessible for sorption, representing the chief attenuation mechanism for contaminant transport in this context.

![Breakthrough of bromide, fluorescein, and lithium (tracer test III). Tracer input was continuous over a time step from t = 0 - 354 hours. Recovery (%) in brackets. Logarithmic time scale.](image-url)
LABORATORY INVESTIGATIONS

To supplement the field tests, laboratory diffusion experiments and batch sorption experiments are being conducted in order to independently quantify the relevant parameters (diffusion coefficient, partition coefficient, sorption isotherms, etc.) for selected substances and rock samples from Münchehagen. Particular priority is given to investigating site-specific organic compounds of environmental concern. The rock samples used were obtained from drill cores from the Münchehagen site. The samples were vacuum sealed immediately after collection and were cooled and stored in airtight containers. The test liquids were provided by collecting genuine formation water, which was not brought into contact with the air and was stored in an inert atmosphere (argon).

The diffusion experiments are being conducted using radioactively labelled test substances in specially designed double cells (Fig. 8). The substances considered are: Tritiated water and aqueous phase solutions of $^{14}$C-benzene, $^{14}$C-chloroform, $^{14}$C-1,4-dichlorobenzene, and $^{14}$C-benzoic acid, each being diluted with genuine formation water. Extra care is being taken in handling the rock samples to avoid deterioration of any kind. To avoid volatilization of the test substances and to inhibit losses due to biotransformation during testing, the diffusion apparatus is kept airtight and an inorganic mercury compound is added as biocide. The tests are being performed as triplicates. Additionally, a blank test is being performed to be able to allow for losses due to sorption on the walls of the diffusion cell. The test substances (a single substance in each experiment) are added to one chamber of the diffusion cell. Molecular diffusion occurs through the rock sample into the

![Diagram of the experimental setup used for the diffusion experiments.](image-url)
opposite chamber due to the concentration gradient across the rock sample. The variation in concentration with time in both chambers is recorded. The concentrations are measured via radiation with a liquid scintillation counter. So far, only the results of the experiments conducted with tritiated water are available (Fig. 9). The effective diffusion coefficients \( D \) have been determined from the slope \( \frac{\Delta C}{\Delta t} \) of the linear section of the breakthrough curve by:

\[
D = \frac{V L}{C_0 A} \frac{\Delta C}{\Delta t}
\]

derived from Fick's second law of one-dimensional diffusion assuming that the initial concentration \( (C_0) \) has not changed significantly (Meier et al., 1988); \( V \) is the volume of the chamber, \( L \) and \( A \) are the thickness and the cross-sectional area of the rock sample, respectively.

The sorption experiments are being conducted using the much practised batch equilibrium procedures. They are intended to supplement the field tracer and laboratory diffusion tests. Sorption coefficients are being determined and compared to the values determined from the diffusion experiments. In addition non-ideal sorption behaviour due to kinetically controlled sorption, isotherm non-ideality and sorption-desorption non-singularity are being evaluated with respect to their relative significance and their potential impact on the contaminant transport at the Münchehagen site. The tests are being carried out using formation water and ground homogeneous rock samples, comparable to the samples that are being used for the diffusion experiments.

![Graph](image-url)

**Fig. 9** Diffusion experiments. Concentration-time-curves of tritium breakthrough from 5 individual samples. The straight line indicates a linear fit. Also indicated is the range of calculated diffusion coefficients \( D \).

**OUTLOOK**

The solute transport under the prevailing field conditions is mainly governed by matrix diffusion, sorption, and hydrodynamic processes (advection, dispersion) interacting with each other and depending on the physical and chemical properties both of the rock mass and the solute under consideration. It is not possible to assess the full complexity of the groundwater flow and solute transport characteristics. The investigations have to be focused necessarily on
the principal parameters using the appropriate tests under well defined boundary conditions at different scales with respect to time and size. Building upon the results from:
(a) laboratory batch sorption tests;
(b) laboratory diffusion tests using sorbing and non-sorbing substances;
(c) hydraulic tests;
(d) forced gradient tracer tests using a particle tracer, sorbing and non-sorbing tracers;
(e) groundwater sampling and monitoring of the leachate plume spreading.
A synopsis will provide a thorough understanding of the governing processes and the data needed to quantify solute transport under the prevailing field conditions. Further work is being focused on the evaluation of the interacting transport processes by means of currently available 1-D and 2-D (analytical or semi-analytical) models.

Acknowledgements This work is part of a joint research project supported by the Federal Ministry of Research and Technology "Methods for Studying the Subsurface of Planned, Operated, and Abandoned Waste Disposal Sites" and is financed partly by the federal state of Lower Saxony.

REFERENCES