Research Article

About the Dependence of Breakthrough Curves on Flow Direction in Column Experiments of Transport across a Sharp Interface Separating Different Porous Materials

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Conservative transport experiments with layered porous materials (coarse-grained vs. fine-grained) were performed through experimental cylindrical columns to assess the possible occurrence of interface processes at the discontinuity between media with different hydrodynamic and hydrodispersive properties, as proposed by some authors in the past based on modelling and experimental results. The outcomes of the present work show that, under certain conditions, the breakthrough curves (BTCs) obtained for flow through the coarse-grained and then through the fine-grained media (CtF) or vice versa (FtC) can differ. More specifically, an asymmetric behaviour is observed for cases when the ratio between the column and grain diameters is small. Moreover, the discrepancies between CtF and FtC BTCs are enhanced for low flow rates and low quantity of injected solute.

1. Introduction

Solute transport in groundwater is a phenomenon of paramount importance for several practical applications, such as protection of water resources, remediation of contaminated sites and safety assessment of industrial and nuclear plants and of repository facilities of toxic and radioactive waste. The physical and chemical processes controlling solute transport in geological porous media and, in particular, in heterogeneous media are very complex. Laboratory experiments under controlled conditions are a fundamental mean to infer the basic phenomenological laws and the relevant physical quantities at a small scale, as the first step towards the estimation of the fate of contaminants in the environment. Applications also include oil, water, and gas production and packed bed catalysis reactions.

Most laboratory experiments of solute transport in geological porous media are conducted with homogeneous media. This is the case especially of column experiments, for which usually long and slim columns are filled with relatively homogeneous porous materials and flushed with aqueous solutions.

An example of experiments of transport through layers of different media is reported by Berkowitz et al. [1], who performed experiments with columns filled with two layers of different porous materials, a coarse-grained one and a fine-grained one, separated by a sharp interface. The observed breakthrough curves (BTCs) were not symmetric if the water was flowing first through the coarse material and successively through the fine material (CtF) or vice versa (FtC) can differ. More specifically, an asymmetric behaviour is observed for cases when the ratio between the column and grain diameters is small. Moreover, the discrepancies between CtF and FtC BTCs are enhanced for low flow rates and low quantity of injected solute.
yield larger errors in dispersion measurements, and this effect was attributed to the difficulty in creating a truly homogeneous packing of the beads. On the contrary, fine beads pack more uniformly. Moreover, the values of dispersion measured along the column reach the local value after the discontinuity more quickly (i.e., for distances of few length scales) for the F/T flow than for the C/T one. This behaviour, which is not explained by classical Fickian transport theory, suggests the possible occurrence of some interface process. As the study was not focused on the asymmetry of the BTCs, no evidences of asymmetrical behaviour are reported.

Villarreal [5] performed laboratory experiments on dispersive transport across interfaces. Two series of experiments were performed with two flow cells packed with glass beads of different diameters, while retaining the same diameter ratio across the interface. Both asymmetric and symmetric behaviours were observed depending on the diameters of the glass beads. The experiments were very similar to the ones performed by Berkowitz et al. [1] except for the section of the flow cell which was squared (in this case, \( D \) is equal to the side length). Asymmetric BTCs appear when the diameter of the beads is large compared with the side length of the flow cell section (\( D/d \approx 8 \)), and they have been interpreted as a result of complex pore geometries occurring at the flow cell edges and corners. Some numerical simulations supported the hypothesis of preferential flow paths along the flow wall.

Some of the abovementioned experiments were conducted with a porous medium whose grain diameter can be considered rather big if compared with the internal diameter of the experimental column, with ratios \( D/d \approx 7 \) [1] or \( D/d \approx 8 \) [5]. Several works, cited in the review paper by Delgado [6], have shown that if \( D/d < 15 \), flow variations at the local scale might impact the results of the experiments. Indeed, if \( D/d < 15 \), an increase of porosity along the column wall can be expected from the numerical modelling of the geometry of bead packing [7] which might yield channelling along the column.

On the other hand, several modelling works analysed the effects of the interface between two different media. Besides the works by Marseguerra and Zoia [2, 3], other researchers [8, 9] applied lattice Boltzmann equation methods to assess the effects of interfaces between different porous media on flow and transport. The latter works simulated flow and transport at the pore scale for 3D columns where the mean flow direction is perpendicular to the discontinuity between two porous media characterized by different grain size. Such simulations showed that the resident concentration [8] and the pressure [9] averaged over the plane perpendicular to the flow direction have high gradients in the transition zone between the two porous media. On the other hand, Appuhamillage et al. [10] showed that a Fickian transport yields an asymmetric behaviour of the BTCs when flow direction is inverted.

Unfortunately, despite some modelling evidences, experimental works are not yet fully supporting the occurrence of interface processes. In fact, monitoring an increase of resident concentration due to the contrast of the grain and pore size distribution between two different porous media would require difficult noninvasive measures of concentration at the pore scale, as recognized by Zhang et al. [8].

The aim of the present work is to improve the characterization of BTCs of conservative transport across sharp interfaces between porous media (coarse- vs. fine-grained) and to analyse the effects of the experimental setup, namely, the ratio \( D/d \), and of the flow rate and solute injection on the BTC shapes. In particular, it is expected to find information about the physical conditions which permit to observe asymmetric BTCs for coarse-to-fine and fine-to-coarse flow directions. These objectives can be reached by means of a continuous monitoring of the solute concentration at the outlet of the experimental columns and by performing experiments with flow rates smaller than those of previous works [1, 2].

2. Materials and Methods

This section includes the description of the equipment and materials used to perform the experiments.

2.1. Experimental Setup. Transport experiments were performed under saturated steady flow field conditions through cylindrical experimental columns filled with spherical glass beads. A short description of the components of the experimental setup (Figure 1) is given below.

Transport experiments were performed through acrylic plastic chromatographic columns, Amersham Pharmacia Biotech K 9/30, with inside diameter of 0.9 cm and length of 30 cm. A peristaltic pump (Reglo-Digital MS-4/8-100 by Ismatec) permits to set up a steady flow through the column. The flow rate can vary between 0.001 mL/min and 30 mL/min. In these experiments, two separate channels were used for distilled water and for an aqueous solution in which the tracer is dissolved. The water flow is forced in the upward direction in order to facilitate the removal of possibly entrapped air and to reduce both wall effects and fingering.

A system of three 3-way electrovalves permits to select the liquids to be flushed through the column, i.e., either distilled water or the aqueous solution. Moreover, it allows to create a net front between the flow of distilled water and of the aqueous solution.

A spectrophotometer (Lambda EZ210 UV-Vis by Perkin Elmer) is used to continuously measure the absorbance in the solution outflowing from the column. Measurements are collected every second. The selected flow cell (Quartz SUPERASIL® 178.711-QS by Hellma Analytics) has an internal volume of 30 μL and optical path of 1 cm. The choice was based on the high transmissivity for wavelengths smaller than 320 nm and the required measurement precision. A specific calibration of the response curve (absorbance vs. solute concentration) has been performed before conducting the experiments, so that accurate measurements of solute concentration can be eventually obtained.

A weighting device (EK-6000H by ENCO), with a maximum range of 6 kg and a resolution of 0.1 g, is used to measure the mass of solution coming out from the column, so that it is possible to infer the flow rate and to check the flow stationarity.
The whole system is controlled by a personal computer with specific software tools developed with LabVIEW.

Notice that the sampling time of the spectrophotometer is 1 s, as a consequence, the number of measurements used to draw a BTC is so high that the BTCs appear as continuous lines.

2.2. Porous Materials and Solute. The columns were filled to obtain two layers of 15 cm length of uniformly packed spherical glass beads with different meshes. The characteristics of the glass beads are listed in Table 1. For the purpose of the present study, the beads with smaller diameters are considered as the fine (FF and F) porous material while the beads

**Figure 1**: Scheme of the experimental setup (Contaminant Transport and Nuclear Safeguard Laboratory of the Politecnico di Milano).
with bigger diameters are considered as the coarse (C and CC) porous material.

All the sets of glass beads were processed before packing in order to reduce as much as possible the impurities contained in the matrix. In particular, the beads were repeatedly washed with deionized water with electrical conductivity of 0.4 μS/cm (300 cm³ of water for 30 g of beads); after each washing, a sample of water was collected, and its electrical conductivity was measured. The procedure was repeated until the value of electrical conductivity of the washing water was approximately the same among two successive washings. Then beads were dried at 100°C for 20 hours in an oven.

The adopted tracer solution was a 0.1 M aqueous solution of sodium nitrate, NaNO₃.

Concentration breakthrough curves were collected along time via UV-Vis spectrophotometric measurements (PerkinElmer Lambda EZ 210) at the wavelength of 301 nm in a quartz SUPRASIL flow cell of 30 μL (Hellma). Preliminary measurements confirmed the linearity of the relationship between absorbance and concentration.

### 3. Results and Discussion

#### 3.1. Batch Tests

Absence of adsorption affinities between the washed glass microspheres and the sodium nitrate aqueous solution was checked via static batch experiments and analysis by conductivity measurements (Delta Ohm HD 8706-R1). Batch tests were performed according to the EPA 1995 procedure [11]. Namely, for each test, three flasks were used. One flask was filled with 30 mL of a 0.1 M solution of sodium nitrate. The remaining flasks were filled with 6 g of beads taken from different sets for each flask and again the same quantity of solution as the first flask. The flasks were placed on an orbital shaker running at 150 rounds/minute and kept at a temperature of (20 ± 2)°C. The solutions were sampled after 4 hours, 24 hours, and 48 hours, and their absorbance was measured with the spectrophotometer.

The results were very positive, as the values of absorbance for the samples taken from the flasks filled with beads differed from those for the samples taken from the flask containing only the liquid by less than 0.4%. As a consequence, no adsorption was observed, and this permitted to consider that the effects of adsorption/desorption phenomena during the column experiment could be neglected.

#### 3.2. Column Tests with Homogeneous Media

Porous media were previously characterized, and the BTCs were fitted with CXTFIT [12] in order to obtain the relevant physical parameters. The BTCs have been fitted with very small errors ($R^2 > 0.98$). Table 2 reports the mean values of the parameters obtained through some repetitions of each experiment (up to 4). Experiments were conducted with 0.27 mL/min nominal flow rate, and the effective flow rates were measured for each experiment by weighting the outflow solution. Effective porosity was estimated on the basis of the arrival time of the half height of the BTCs with an error lower than 0.3%. Table 2 reports also the average ratios $D/d$ between the internal diameter of the experimental column $D$ and the mean bead diameter $d$. The effective porosity values found are in line with what is predicted by numerical studies regarding the overall porosity of cylindrical containers packed with spherical particles, which is expected to be 40% when the ratio $D/d$ is relatively high (i.e., $D/d > 20$) [7].

It is worth noting that the parameters fitted with CXTFIT show that the Pelet number ($Pe_L$) was of the same order of magnitude for all the tests and much less than 10, namely, varying between 0.12 and 0.83. Therefore, the intensity of advective and diffusive/dispersive phenomena is quite comparable among all these tests.

Then, some additional tests were conducted with columns filled with homogeneous media with the aim of checking the symmetry of the BTCs when the flow direction was reversed. The pore water velocity was close to 0.02 cm/s; the injection of a 0.1 M solution of sodium nitrate started after 1500 s from the beginning of the test and lasted for 1500 s. The reversal of the flow direction was obtained by turning the same column upside down, so that the flow occurred always in the upward vertical direction.

Figure 2 shows the comparison of the results of two tests conducted with the C sets of beads (with an average diameter of about 350 μm). This is one of the cases, among the four studied bead sets, for which the differences between the BTCs corresponding to different flow directions is more evident. Only small discrepancies between the BTCs for the opposite flow directions were observed that can be considered negligible with respect to the asymmetrical expected behaviour.

#### 3.3. Column Tests with Two-Layer Media

The main tests of this work were conducted by preparing two columns, each one filled with two-layer porous media, i.e., by filling half of the column with a relatively fine-grained material and the remaining half with a relatively coarse-grained material. Namely, the column #1 was filled with FF (fine-grained) and C (coarse-grained) beads, whereas the column #2 was filled with F (fine-grained) and CC (coarse-grained) beads. For both columns, the ratio between the grain diameters of

<table>
<thead>
<tr>
<th>Type</th>
<th>Set code</th>
<th>Diameters of microspheres (in μm)</th>
<th>Porous material</th>
<th>Seller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine</td>
<td>FF</td>
<td>70 to 110</td>
<td>Sodium glass tempered beads</td>
<td>Lampugnani Sabbiatrici</td>
</tr>
<tr>
<td>Fine</td>
<td>F</td>
<td>200 to 300</td>
<td>Sodium glass tempered beads</td>
<td>Lampugnani Sabbiatrici</td>
</tr>
<tr>
<td>Coarse</td>
<td>C</td>
<td>300 to 400</td>
<td>Sodium glass tempered beads</td>
<td>Lampugnani Sabbiatrici</td>
</tr>
<tr>
<td>Coarse</td>
<td>CC</td>
<td>1000</td>
<td>Borosilicate glass beads</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>
the fine and the coarse material is about 1:4, the same as for the experiments of Berkowitz et al. [1] and Villarreal [5]. On the other hand, the ratio $D/d$ is greater than 25 for the coarse-grained layer of the column #1 and close to 9 for the coarse-grained layer of the column #2 (Table 3). The latter value is very close to that of the experimental setup adopted for some of the abovementioned experiments [1, 5] (see also Table 4).

For each column experiment two BTCs were obtained: one when flow occurred through the coarse-grained material and then through the fine-grained material (CtF: coarse-to-fine) and one when flow occurred in the opposite direction (FtC: fine-to-coarse) direction (Figure 3). Several experiments were conducted by varying the flow rate and the quantity of injected solute. At first, two experiments were conducted with column #1 at two different regimes of flow, i.e., 0.27 mL/min and 0.09 mL/min and with source term equal to 1.5 mL. In both cases, it was not possible to recognize any significant asymmetry between the CtF and FtC BTCs, as shown in Figure 4.

Afterwards, three experiments were performed with column #2 at three different flow rates (0.27 mL/min, 0.09 mL/min, and 0.054 mL/min) and with a varying duration of the injection of the 0.1 M solution of sodium nitrate, so that the same amount of solution (2.7 mL), and therefore of solvent (sodium nitrate), is injected. The results are shown in Figure 5 (see also Figure S1 of the Supplementary materials) and clearly show some discrepancies between the BTCs for the CtF and FtC flow directions. Such differences are negligible for the highest flow rate (0.27 mL/min), appear for the intermediate flow rate (0.09 mL/min), and are very evident for the lowest flow rate (0.054 mL/min).

In order to assess the possible effect of the injected quantity of solute, the same experiments performed with column #2 were repeated but with a reduction of the amount of solution injected by almost a factor 2 (1.5 mL). The results are shown in Figure 6 (see also Figure S2 of the Supplementary materials) and demonstrate that the experimental setup adopted for some of previous experimental studies and cover a wide range of values of the ratio $D/d$ and low flow rates. Of course, in order to inject the same amount of sodium nitrate, the duration of the injection of the 0.1 M solution of sodium nitrate was varied. The results are shown in Figure 7 (see also Figure S3 of the Supplementary materials) and clearly show no discrepancies between the BTCs for the CtF and FtC flow directions.

### 4. Discussion

In order to facilitate the comparison between the results shown in this paper and in previously published experiments of transport through two-layer porous media [1, 4, 5], some basic data about the experimental setup are listed in Table 4. It is apparent that the experiments considered in this paper were designed with the goal of sharing characteristics similar to some of previous experimental studies and cover a wide range of values of the ratio $D/d$ and low flow rates.

The experiments conducted in this work with $D/d > 15$ (column #1) do not show any asymmetry between CtF and FtC BTCs. Some discrepancies occur, instead, when the above condition is not satisfied and for low flow rates, in agreement with published results [1, 5].

The behaviour of the BTCs is systematic through all the conducted experiments: peak concentration is higher for the FtC BTCs, whereas the tail is longer and with a higher concentration for the CtF BTCs. Such behaviour is enhanced at low flow rates and for reduced quantities of injected solutes. These remarks are in agreement with the results of models based on Fickian theory [10].

However, it should be stressed that the discrepancies between CtF and FtC BTCs often appear as a change of

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### Table 2: Data regarding characterization of the porous materials and performed experiments with homogeneous column.

<table>
<thead>
<tr>
<th>Code of porous material</th>
<th>Diameters of microspheres (in μm)</th>
<th>Effective porosity</th>
<th>Pore velocity (in cm/s)</th>
<th>Dispersion coefficient (in cm$^2$/s)</th>
<th>Dispersivity (in cm)</th>
<th>Peclet number</th>
<th>$&lt;D/d&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FF</td>
<td>70 to 110</td>
<td>40.2%</td>
<td>0.0175</td>
<td>$1.32 \times 10^{-3}$</td>
<td>0.075</td>
<td>0.12</td>
<td>100</td>
</tr>
<tr>
<td>F</td>
<td>200 to 300</td>
<td>38.0%</td>
<td>0.0196</td>
<td>$8.22 \times 10^{-4}$</td>
<td>0.042</td>
<td>0.60</td>
<td>36</td>
</tr>
<tr>
<td>C</td>
<td>300 to 400</td>
<td>40.3%</td>
<td>0.0175</td>
<td>$7.3 \times 10^{-4}$</td>
<td>0.042</td>
<td>0.83</td>
<td>26</td>
</tr>
<tr>
<td>CC</td>
<td>1000</td>
<td>40.1%</td>
<td>0.0182</td>
<td>$2.26 \times 10^{-3}$</td>
<td>0.124</td>
<td>0.81</td>
<td>9</td>
</tr>
</tbody>
</table>

![Figure 2: Breakthrough curves of experiments with a homogeneous column—300-400 μm beads. Flow rate = 0.27 mL/min. Test 1 and 2: direct tests; test 1R and 2R: reversed column tests.](image)
convexity of the BTCs (Figures 5 and 6). This effect is not explained by the results of Fickian models, whereas it is typical of transport in dual domain media (see, for instance, Baratelli et al. [13, 14]). Since this behaviour is observed in the experiments for the smallest value of $D/d$, it might suggest that a preferential flow path occurs along the side of the column. In fact, the arrangement of the grains with relatively high diameter cannot avoid the creation of relatively large pores at the contact with the wall of the experimental column.

Although a more accurate interpretation requires a thorough modelling and further experimental tests, the results of this work support the remark that occurrence of asymmetrical BTCs in two-layered media depends also on the experimental setup, in particular the $D/d$ ratio. However, if any physical process occurs at the interface between media with different grain size, and therefore different hydrodynamic and hydrodispersive parameters (porosity, permeability, and dispersivity), it should be more apparent at low flow rates.

5. Conclusions

This work shows the results of experiments aimed at assessing the occurrence of physical processes which might affect solute transport in groundwater at the interface between media with different grain size, i.e., at discontinuities between sediments characterized by different hydrodynamic and hydrodispersive parameters.

The column tests were performed under an accurate procedure in order to manage possible effects due to preferential flow paths along the border of the columns or to fingering. The high-frequency measurement of solute concentration in the outflowing solution with a spectrophotometer permitted to obtain high-quality and practically continuous BTCs. The results of this work show the relevance of the experimental setup to evidence the effects of possible interface processes. Such effects appear when the ratio between the inner radius of the column and the grain size was quite small, and it was more clearly evidenced by tests with low flow rates and low quantities of the injected solute.

In order to emphasize the possible interface processes, it could be important to work with columns where the diameter-to-length ratio is large. Notice that in this case and in the similar works published in the scientific literature (see Table 4) [1, 4, 5], this ratio varied between 3% and 7%, which is quite small. Of course, working with short

Table 3: Characteristics of the two-layer media columns.

<table>
<thead>
<tr>
<th>Column number</th>
<th>Length (in cm)</th>
<th>Internal diameter (in cm)</th>
<th>Diameters of microspheres (μm) F (fine) section</th>
<th>C (coarse) section</th>
<th>Ratio between mean diameters of spherical beads</th>
<th>$&lt;D/d&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column #1</td>
<td>30</td>
<td>0.9</td>
<td>70 to 110</td>
<td>300 to 400</td>
<td>3.9</td>
<td>100 &amp; 25</td>
</tr>
<tr>
<td>Column #2</td>
<td>30</td>
<td>0.9</td>
<td>200 to 300</td>
<td>1000</td>
<td>4</td>
<td>36 &amp; 9</td>
</tr>
</tbody>
</table>

Table 4: Characteristics of the glass beads used for the experiments in two-layer media.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.3 to 1</td>
<td>0.3 to 3</td>
<td>0.3 to 3</td>
<td>2.2 to 5.4</td>
<td>0.003 to 0.27</td>
<td>0.054 to 0.27</td>
</tr>
<tr>
<td>Column length $L$ (in cm)</td>
<td>40</td>
<td>47</td>
<td>47</td>
<td>100</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Inner column diameter $D$ (in cm)</td>
<td>2.7</td>
<td>3.18</td>
<td>3.18</td>
<td>3.2</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>$D/L$</td>
<td>0.068</td>
<td>0.068</td>
<td>0.068</td>
<td>0.032</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Grain type*</td>
<td>F</td>
<td>C</td>
<td>F</td>
<td>C</td>
<td>F</td>
<td>C</td>
</tr>
<tr>
<td>Average grain diameter $d_F$, $d_C$ (in mm)</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>0.25</td>
<td>1.63</td>
</tr>
<tr>
<td>Ratio between mean diameters of beads $d_C/d_F$</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>3.6</td>
<td>3.9</td>
<td>4</td>
</tr>
<tr>
<td>Dispersivity (in mm)</td>
<td>1.3</td>
<td>9.6</td>
<td>N/A</td>
<td>N/A</td>
<td>0.035</td>
<td>0.175</td>
</tr>
<tr>
<td>$D/d$</td>
<td>27</td>
<td>7</td>
<td>32</td>
<td>8</td>
<td>127</td>
<td>32</td>
</tr>
<tr>
<td>Peclet number ($Pe_L$)</td>
<td>0.77</td>
<td>0.42</td>
<td>N/A</td>
<td>N/A</td>
<td>4.6</td>
<td>3.4</td>
</tr>
</tbody>
</table>

*F: fine; C: coarse.

Figure 3: Sketch of the flow directions for the CtF and FtC experiments.
columns with a large diameter could introduce difficulties to guarantee that flow and transport occur under one-dimensional conditions, i.e., without an excessive perturbation of a one-dimensional flow and transport field caused by heterogeneities at the microscopic (pore and grain) scale.

**Data Availability**

Data will be available upon request to the authors for collaborative research projects.

**Conflicts of Interest**

The authors declare that there is no conflict of interest regarding the publication of this paper.
Acknowledgments

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Supplementary Materials

The supplementary material includes plots of the breakthrough curves shown in Figures 5, 6, and 7 as a function of pore volume. *(Supplementary Materials)*

References


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