Experimental study of solute transport in a carbonate porous media

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Abstract

More than 40 % of carbonate area in Slovenia and development of urban activities, which cause the pollution lead to more frequent researches of solute transport in fractured and karstified rocks.

The laboratory experiments were made to study the behaviour (sorption) of tracer in a porous media as preliminary study for in-situ tracer experiments in fractured rocks and final modelling of mass transport. The experiments in saturated zone were carried out in the laboratory of the Institute for Mining, Geotechnology and Environment in three permeameters which were connected successively. There also existed a possibility of sampling after each permeameter. As media there were used three porous materials of different grain size distribution from a close limestone quarry. Salt and uranine were used as tracers. During the tests various measurements like flow, pressure, temperature, pH, conductivity, oxygen content, alkalinity, acidity and uranine content were constantly performed. So far are the results undetermined due to detection problems, so we were forced to perform additional batch-tests to confirm the sorption process. The experiments in a physical model, where unsaturated zone would also be researched, are planned.

In-situ experiments were done between a surface and a research tunnel in fractured carbonate rocks. First of all, a precise cartography of the fractures on the rocks over the tunnel and within the research tunnel was performed. Holes for injecting the tracers were located on the basis of the 3-D definition of the fractures between the surface and the research tunnel. The flow rate of the tracer was estimated by measuring the descending tracer concentration in the research tunnel. The tests were made to obtain different paths of water and the distribution of residence time of the tracer. The results of laboratory and in-situ experiments will be used as the input data for a final mass transport model.
1 Introduction

The main goal of this research was the study of mass (pollutant) transport in fractured and karstified carbonate rocks, particularly in the unsaturated zone [15]. To our knowledge investigations in fractured and karstified rocks have not been made previously on such scale [14], [15]. However, similar investigations have been performed in experimental mines in Sweden and France for the purpose of radioactive waste disposal [1],[2],[4]. Our second important objective was a comparison of the results of modern structural analysis developed for the purpose of regional groundwater flow determination, allowing a surface outcrop analysis and a local flow pattern determination requiring an excavation wall analysis.

In the first phase the laboratory experiments were performed, comprising relations of flow to permeability, porosity, active rock surface, representative elementary volume (REV), art of the rock, water and tracer and rock saturation [15]. At the same time a structural analysis of the Sinji Vrh in-situ ground, large enough to make up for REV, was performed. In the second phase a special in-situ ground was used for tracing experiment. All data gained from the laboratory and in-situ experiments will be used in final modelling of mass transport.

2 Laboratory experiments

2.1 Experimental design

During the laboratory test we examined tracers which were used later in terrain experiments on porous karst limestone. We were particularly interested in behaviour of the tracer during the flow through the karst rock - especially the sorption of both tracers used: NaCl and uranine. The first tracer does not react with a rock [6] and the second one belongs to the group of fluorescent dyes that are prone to sorption [7].

Table 1: Permeameter experiment schedule - experimental design

<table>
<thead>
<tr>
<th>Moistening</th>
<th>Tracer solution</th>
<th>Tracer solution</th>
<th>Granulometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 DM H₂O</td>
<td>NaCl+ DM H₂O (MF)</td>
<td>uranine(HC)+ DM H₂O (HF)</td>
<td>G1</td>
</tr>
<tr>
<td>2 DM H₂O</td>
<td>uranine(HC)+ DM H₂O (MF)</td>
<td></td>
<td>G1</td>
</tr>
<tr>
<td>3 dry sample</td>
<td>uranine(LC)+ DM H₂O (LF)</td>
<td></td>
<td>G1, G2, G3</td>
</tr>
<tr>
<td>4 dry sample</td>
<td>NaCl+ DM H₂O (LF)</td>
<td>uranine(LC)+ DM H₂O (LF)</td>
<td>G2, G3</td>
</tr>
<tr>
<td>5 dry sample</td>
<td>uranine(HC)+ DM H₂O (LF)</td>
<td></td>
<td>G2</td>
</tr>
<tr>
<td>6 dry sample</td>
<td>uranine(HC)+ DM H₂O (LF)</td>
<td>demineralised H₂O</td>
<td>G3</td>
</tr>
<tr>
<td>7 dry sample</td>
<td>uranine(HC)+ natural H₂O(LF)</td>
<td></td>
<td>G2</td>
</tr>
</tbody>
</table>

DM=demineralised H₂O, HC=high concentration (about 1mg/m³), LC=low concentration (about 0,1mg/m³), LF=low flow (22,7-34,3 l/h), MF=mid-flow (41,1; 55,8 l/h), HF=high flow (110,4 l/h), G1=sample 1 (0,160-4mm), G2=sample 2 (4-8mm), G3=sample3 (0,160-8mm).  

The main goals of the experiments were to determine the sorption of the uranine on the limestone samples and to determine the effects of water flow through unsaturated media (moistening of dry limestone samples) on uranine sorption on the limestone [15]. Limestone grains from Razdrto quarry were used as approximation of the carbonate rock from Sinji Vrh. Additional tasks were to determine relation of grain surface to residence time of uranine solution in limestone sample. The experiment schedule is shown in table 1.

2.2 Experimental system

2.2.1 Description of experiment system
Experiments were performed at the Institute for Mining, Geotechnology and Environment. Experimental system consisted of three equal permeameters, each 1.5 m long with a diameter of 15 cm which were sequentially interconnected (figure 1). At the end of each third of these series, that is, at the end of each single permeameter, fluid sampling was possible. The flow has been restored naturally. Lineal and constant flow has been enabled by large 100-l-collecting reservoirs (figure 1) containing fluid which maintained constant hydraulic predetermined head through pouring of liquid.

![Figure 1: Experimental system.](image)

![Figure 2: Grain-size curves for three samples.](image)

2.2.2 Characterisation of material
Permeameters have been filled with limestone granulate of various grain sizes. Samples from Razdrto quarry with technical signatures of 0/4 and 4/8 have been used. Because of an excessive amount of experiment samples necessary, samples could not have been taken directly on terrain, where the field tracing experiments were carried out.

The fraction under 0.160 mm has been removed from the sample 0/4 (from 0 to 4 mm) through rinsing of particles and the first sample of granulation between 0.160 - 4 mm was thus obtained. Granulate 4/8 (4-8 mm) has been taken as a sample 2 and a sample 3 was obtained through the combination of both samples in ratio 1:1 (0.160 - 8 mm) [16]. Figure 2 depicts granulometric analysis by sifting all three samples.
Limestone granulate has been taken from Razdrto quarry which is also situated on karst terrain. Sample from the quarry is close to pure limestone and contains 99.3% of CaCO₃. The rock from the first locality (Unška Koliševka) of in-situ test ground is pure limestone containing 99.4% CaCO₃ while on the second (Sinji Vrh) in-situ ground next to the limestone of 99.3 - 99.6 CaCO₃ there also exists dolomitic limestone (35% CaCO₃ and 65% MgCO₃).

2.2.3 Properties of the flow through the rock samples

During the experiment we wanted to study the laminar flow through the rock sample, so the Reynolds value had to be lower than 10 [3].

Permeability coefficient $k$ of single rock samples was calculated using empirical equation USBR [12] which takes into account effective grain diameter ($d_{20}$ in mm) from granulometric curves (figure 2):

$$k_{USBR} = 0.36 \times (d_{20})^{2.3} \times 10^{-3} \text{ [m/s]}$$

For the first sample the permeability coefficient was $1.2 \times 10^{-4}$ m/s, the second $1.5 \times 10^{-2}$ m/s and for the third one $5.2 \times 10^{-4}$ m/s. For each sample the highest hydraulic head $\Delta h$ was calculated, where the flow remained laminar. We could have optional hydraulic head in the first (4.08 m) and the third sample (0.5 m). In the second sample the hydraulic head was only 0.1 m (the flow has been hindered on 30 l/h) [5],[16].

2.2.4 Applied tracers

NaCl and uranine have been used as tracers. NaCl is a salt that is very easily dissolved in water (358.5 g/l at 20°C) and dissociates on Na⁺ and Cl⁻ ion. Cations are subject to ionic interchange regarding the ion concentration reduction. During this process the other ions bond due to established balance of charge - creators of hardness [7]. Since anions do not react with the rock, their concentration better describes the flow through the rock [6]. During the experiment NaCl was used as a comparison of sorption with uranine and we have measured only conductivity.

Fluorescent dye uranine is a sodium fluorescein which has a structural formula $C_{20}H_{14}O_{5}Na_2$. Fluorescein anion form is at present the best known fluorescent substance and has thus been the most useful tracer for an extended period of time. Fluorescent dyes have various sorption properties on rocks. Generally the cation dye form is more subject to sorption than anionic form. Uranine cation has also sorption properties, so alcaline media and anionic uranine form is requested. At the same time, the intensity of fluorescence is higher in alcaline media [7].

During the experiment NaCl concentration of $10^3$ mg/m³ and uranine concentrations 0.1 and 0.01 mg/m³ were used. Demineralised water was used as a media in order to provide similar circumstances compared to those in the nature, where rain leaks through the rock. In one experiment the natural karst water from Malni spring was also used (table 1, No. 7).

2.3 Experimental process

During the experiment permanent measuring of flow (flow meters) and pressure (Hg manometers) in permeameters has been carried out. Gained samples were
measured with laboratory instrument - temperature, pH, conductivity and oxygen content. Acidity and alkalinity have been determined at our Institute using the ASTM method. Content of uranine in samples was determined at the Institute For Karst Research, ZRC SAZU.

14 experiments were carried out (table 1) on experimental system described above and one on a smaller experimental system (glassy columns 0.5 m high with diameter of 0.055 m). The succession of experimental phases and experiment systems are schematically shown in table 1. The first column describes the art of moistening, the second column tracer solution and used media (demineralised water and natural karst water from Malni spring). The fourth column depicts sample grain size. Each experiment performed on the same system with low concentration was first carried out using NaCl, then followed by uranine, and ended up with a study of interactions between tracers (table 1, No. 1,4).

In the experiments from number 3 to 7 (table 1) constant flow sized from 22.7 to 34.3 l/h was sustained; except at the small system (table 1, No.7), where the flow was calculated for small system (equivalent for other system with low flow). All experiments were performed with permanent in-flow of fresh solution until the balance was restored. During the last experiment (table 1, No.6) a clear demineralised water was added after a determined time and after circulating a constant tracer concentration.

Batch tests were carried out in large 100 l reservoirs to provide enough volume of samples. Experiments were carried out to determine commutation of content of $\text{Ca}^{2+}$ and $\text{HCO}_3^-$ ions, uranine, acidity, alkalinity, and other parameters (particularly pH and conductivity). Demineralised water and natural karst water from Malni spring was used as a media. For the limestone samples only the granulation of 0.160-8mm (third sample) was considered.

2.4 Results

2.4.1 Results of tests with NaCl solution

For the NaCl experiments the conductivity measurements were predominant (table 1, No. 1, 4). The conductivity has raised at the beginning of the experiment because of the dissolution of the limestone and stabilised at a value a little bit higher than value of the initial NaCl solution when limestone dissolving equilibrium has been attained [5],[17]. The figure 3 shows the conductivity of NaCl solution samples (left of the vertical line) after the 3rd permeameter (full line) and initial concentration ($0.98*10^5$ mg/m$^3$) of NaCl solution in demineralised water (hatched line). Right from the vertical line is the conductivity of the uranine solution (full line) and initial uranine solution (hatched line) in demineralised water (table 1, No.4, G2).

2.4.2 Results of tests with uranine solution

The results of experiments with small uranine concentration (round 0.1 mg/m$^3$) were inconclusive due to various errors (analytical, problems with the cleaning of the permeameters) and because of some results that were higher than initial value (figure 4). At experiments with higher uranine concentration (round 1
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(round 1 mg/m$^3$) such difficulties did not appear [5],[17]. The uranine concentration remained more or less constant during the experiment (figure 5). A fall of concentration (time about 24 and 48 hours) was due to higher retardation time (velocity drops during the night time).

Figure 3: The conductivity of NaCl solution samples (left of the vertical line) and of the uranine solution (right from the vertical line).

Figure 4: Breakthrough curve for uranine for system 6 (4/8mm, uranine concentration: 0,094 mg/m$^3$) and system 9 (0,160/8mm, 0,095 mg/m$^3$).

The last experiment (table 1, No. 6) was not performed like other experiments - after moistening with uranine solution the initial solution was replaced with pure demineralised water. The uranine solution in the permeametres was quickly replaced with pure water, that shows rapid reduction of uranine concentration (figure 6). In batch test the uranine concentration slightly oscillates around initial uranine concentration similar to the experiments in permeameters.

Figure 5: Uranine breakthrough curve (4/8 mm, uranine concentration: 0,941 mg/m$^3$).

Figure 6: On the left side of vertical line: uranine breakthrough curve (0,160/8 mm, 0,938 mg/m$^3$). Right side: initial uranine concentration replaced with pure demin. water.

2.5 Conclusions

A final conclusion could not be drawn for experiments with low uranine concentration (about 0.1 mg/m$^3$), due to inconsistency of the results (the sum of errors: analytical, sampling, cleaning the system and sampling material). In
A perceptible uranium content was obtained in samples not containing uranium. Experiments with high uranium concentration (about 1 mg/m³) gave better results. The sorption of uranium was negligible and uranium is usable in in-situ tracer experiment. Regarding precision of experiments the sorption depended on active grain surface and contact time of uranium solution and limestone sample from Razdrto quarry, which confirm diminishing of uranium concentration in the times of low velocity (larger contact time solution-sample).

The rate of specific sorption in the last experiment system (sample 3, figure 6) was possible to estimate from flow, duration of the experiment and diminishing of uranium concentration. Considering the 5.5% of diminishing of uranium concentration 0.938 mg/m³, flow 23.8 l/h, duration time 4.5 hours and the specific grain surface 387 m² the rate of specific sorption was 3.2*10⁻⁶ mg/m²h. This applied to the limestone from Razdrto quarry and there was a simplification to the sphere grains. Considering the Heywood factor 1 - 2 the rate of specific sorption was in range from 1.6*10⁻⁶ to 3.2*10⁻⁶ mg/m²h. Exact calculus demands additional analysis of sphericity. This rate of specific sorption is an indication only, because it was calculated only from one experiment system (table 1, No.6). In other experiments the results were either inconclusive or there was no diminishing of uranium concentration due to the lack of sensitivity of the method. Therefore, the last experiment was carried out in a different manner (table 1, No.6). This result demands a repetition of experiments to verify the conclusion of the rate of specific sorption.

When moistening limestone with uranium solution in demineralised water the sample bound water caused initial reduced retardation of uranium concentration drop because of negligible uranium sorption. In experiments with low concentration this effect could not be reliably established. By decreasing the flow through limestone sample in permeameters the residence time increased and diffusion and sorption processes became perceptible (diminishing of uranium concentration in figure 9), as in the case where the specific grain surface (sample 2) was smaller than in the last experiment system. Yet no rate of specific sorption determination was attempted due to the possible masking effect of diffusion (within the retention porosity volume).

3 In-situ experiments

3.1 Experimental design

In fractured karstified rocks experiments in unsaturated zone have not been made previously. Experiments in unsaturated zone in Slovenia were made only to determine the connection between the surface pollutants and karst caves [8],[9].

Correlation between structural analysis of the surface outcrops and within the tunnel was determined by detailed mapping of fractures on two in-situ grounds in Slovenian karst region (Unška Koliševka and Sinji Vrh). The criteria for ground selection were the existence of an underground tunnel, the subsurface depth of the tunnel, viability (experimental costs to success expectancy ratio) and the major one - the nature of karst rock in conformity with the REV criterion [13]. Owing to special geological circumstances and predetermined paths, there was also a special criterion: absence of karst caves.
The locality of Sinji Vrh was chosen for tracer experiments, where a tunnel exists under 10-13 metres of rock cover. From the fracture mapping at the surface and within the research tunnel we could properly position injection holes, which were positioned above the tunnel crossing (figure 7), where the area is grassy. The holes were drilled only through the soil cover to avoid fracture flow disturbancy within the rock and to allow for elimination of parasitic surface soil cover effects. A special construction for collecting water penetrating through the rock was developed.

![Figure 7: The position of the surface rock area and research tunnel](image)

The aims of the experiment were to determine parameters of vertical flow through variably saturated fractured rock, to obtain relations of flow to fracturation and bedding parameters and to identify the flow and transport properties in the unsaturated limestone rock.

### 3.2 Experimental system

#### 3.2.1 Characterisation of experimental system

A special water collecting structure was made in our Institute and installed into the tunnel. One link of the construction consisted of metal girders on which a plastic sheet was tightened. Special funnels were made to collect water seeping from the rock in narrow sampling containers (figure 8). The water was gathered from the ceiling of the tunnel and also from the upper part of the walls in 1.5 m long segments with a gathering surface of 2.2 m². The total length of the collecting area was 43 metres with interruption of 7 metres due to dry rock.

![Figure 8: Construction for collecting water samples](image)

#### 3.2.2 Characterisation of material

In the investigated area there is a fault zone at the crossing of the tunnels. In this zone the limestone is dolomitised and contains 35% CaCO₃ and 65%
MgCO₃. The rock in the dead end and access tunnel is almost pure limestone containing 99.5% CaCO₃. In the laboratory experiments material out of the fault zone (pure limestone) was chosen. For the evaluation of tracer experiments in the fault zone additional experiments should be done.

![Figure 9: Ground plan of the fractures in the research tunnel](image)

Detailed study of the fractures was performed twice. First a statistical analysis of the fractures was made in the wet period (autumn), where various parameters like art of discontinuity, orientation (dip), extension, thickness and aperture, nature of the filling material, roughness, weathering and water flow were measured [10], [13], [16]. Afterwards, a detailed mapping of the fractures of the surface outcrops and within the research tunnel was carried out. Figure 9 depicts ground plan of the mapped fractures in the research tunnel. The main fracture and fault strike of the surface rocks and within the tunnel is NNE-SSW (295/80 and 115/85), the subordinate dips are 85/40-90, 185/85, 140/80. The dip of limestone strata is 230/14-50. Injection holes were located above the crossing, because the most part of the fractures are subvertical (figure 10). A possible influence of the strata on the water flow through the rock could be observed in the tunnel SW of the crossing.

3.2.3 Applied tracers

First a preliminary experiment was performed to obtain main flow characteristics. Due to simple detection NaCl was used as tracer. To get more information about flow conditions, another experiment with NaCl and KCl as tracers will be executed. We plan to use more tracers (NaCl, KCl, uranine, rhodamine) in the main experiment to confirm flow distribution and transport properties. In different boreholes various tracers will be injected. Due to the circumstances only the first experiment was carried out.

3.3 Experimental process

The tracer was injected in 18 holes at the surface area above the tunnel (figure 7). We decided to perform momentary injection not to risk a concentration drop under detection limit at continuous injection [7]. After the injection a grassy area was dosed with approximately 420 l water to hasten a process and simulate rain. Water seeping from the upper part of the tunnel was gathering in sampling
containers of each segment. Samples were measured with portable instrument (temperature, pH and conductivity). Water quantity was only evaluated (water level in container). Ca\(^{2+}\), Mg\(^{2+}\), HCO\(_3\)\(^{-}\) (alkalinity, acidity) and Cl\(^{-}\) ion contents were determined at our Institute. Due to short distance and intense fractured rock measurements were made in small intervals (half hour at the beginning and 5 hours at the end of the experiment). There was weekly control after the experiment was carried out.

Figure 10: Vertical cross-section BB* (regarding to figure 9)

3.4 Results

Tracer has appeared only in two segments (number 4 and 5 in figure 9) shortly after the injection [17]. Tracer breakthrough curve for sampling segment No. 5 is illustrated in figure 11. It is normed at the highest value, since a better presentation was our goal.

The peak values after the first tracer breakthrough (c/c\(_0\)=0.75 and 0.5) have occurred because the meadow above the tunnel was additionally watered (time of 20 and 55 h). Subsequently it started to rain (time of 58 and 103 h). Without watering, the breakthrough curve would probably look like the hatched line in figure 11. Watering of the surface was done in order to simulate the fastest possible vertical flow, which is very important for determining an intervention time in the case a pollution occurs. Additionally, it should allow to observe an eventual flow dispersion and flow retardation resulting from the observed fracture and bedding plane pattern and control by other sampling segments.

For determination of the dispersivity coefficient a method of Sauty [7] was used. With layering of the breakthrough curve, normed to the minimal concentration of 0 and maximal concentration of 1 and the type-curve for various Peclet numbers, we could get real flow velocity. In our case Peclet number was 1.5 and real time 4.5 hours. Considering the flow path (X) of 10 metres real flow velocity (v\(_a\)) was 2.2 m/h. Regarding equation (2) for longitudinal dispersivity coefficient D\(_l\) [7] its value was 15 m\(^2\)/s:

\[
D_l = \frac{v_a \cdot X}{Pe}
\]  

Figure 11: Conductivity distribution of water samples in segment No.5
3.5 Conclusions

Tracer experiment indicated one fast path channel, where water runs faster than in the total conductive part of the rock. In our case the main flow structure was a fault in the access tunnel (figure 9). This fact is not enough to design a flow in fractured rock in general, but we should be aware, that such direct and fast paths exist in karst and are very important in determining potential pollutant locations. This experiment is the first evaluation of flow conditions in the research area. Beside this channel we would also like to determine flow conditions for the entire observed fractured rock mass (longer residence time) for which additional experiments will be executed. Concerning the watering or rain induced concentration increments in the tunnel inflow, it is apparent that the observed breakthrough time after start of watering was 4.5-5 hours and after start of raining 2-5.5 hours. We attribute this difference to the time needed for soaking of the surface soil cover. Only 4.5 hours are necessary for the flow through the tunnel rock overburden. Yet the actual rock saturation is preponderably influencing this figure, which is true only for the complete rock saturation. Saturation rate was not measured, however, due to snow melting it was very high. It is obvious that the stratification impact on the water flow is more important than generally believed. Additional boreholes will be drilled to provide additional control of this fact. After the definition of flow characteristics of the affected rock mass main experiment with more tracers will be performed.

It must be noted that only addition of new fresh water (let it be from watering or raining) results in additional rinsing of pollutant, provoking a temporary raise in its concentration. We have still to determine, whether the pollutant is retained in the surface soil cover or small fractures of the overburden rock mass. However, given the nature of the observed, we believe that it is retained and gradually rinsed from the surface soil cover.

The first experiment was performed in heavily fractured zone, which is not relevant for fractured rock in general, but characteristic of principal groundwater alimentation paths within the vadose zone of karstic aquifers. An experiment in dry time period would be very interesting for determination of the difference among tracer recovery (mass through flow), residence time and flow velocity.

4 Acknowledgement

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References


14. Veselić, M. 1995b: Il moto ed il transporto nei mezzi fratturati come il base per il controllo dell’inquinamento (Flow and Transport in Fractured Media as a Basis for Pollution Control), in Propagazione di inquinanti in sistemi porosi e fessurati, ed. S. Troisi, 231-284, TECHWARE, BIOS, Cosenza, Italy.

