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Comparison of water phase diffusion experiments in the in-situ and laboratory conditions

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Abstract

In some countries, the spent nuclear fuel produced by nuclear power plants will be deposited in crystalline granitic rock formations. In Finland, such repository is being built at Olkiluoto. The safety assessment of the repository requires a careful determination of transport properties of the bedrock. Porosity of the rock and effective diffusion coefficient and distribution coefficients of different radionuclides for the bedrock are used as the main parameters in safety assessment calculations. It has been questioned if the parameters determined using laboratory experiments can be used to estimate the parameters in the in-situ conditions. Water Phase Diffusion Experiments (WPDE) performed in the laboratory and in-situ conditions were addressed to resolve this questions. In the experiments, transport of HTO, ^{36}Cl and ^{22}Na were studied using similar experimental setups in both conditions. Analytic models were constructed and solved to determine the transport parameters from the measured breakthrough curves. The in-situ WPDE resulted from 12 % to 38 % smaller porosities and from 30 % to 60 % smaller effective diffusion coefficients for HTO and ^{36}Cl than the laboratory WPDE. It was also shown that anion exclusion reduced the transport parameters of ^{36}Cl compared with the parameters of HTO in veined gneiss that is the most dominant rock type of Olkiluoto bedrock. Furthermore, the distribution coefficients of ^{22}Na for veined gneiss were found to be about one order of magnitude smaller in the in-situ conditions than in previous laboratory batch sorption experiments. The effects of the results on the safety assessment were evaluated and discussed.

Keywords: in-situ experiment, diffusion, sorption, porosity, radionuclide

1. Introduction

In some countries, the spent nuclear fuel produced by nuclear power plants will be disposed in crystalline rock formations. Such repository is being built at Olkiluoto Island (Eurajoki, Finland). The concept consists of multiple transport barriers that include a copper canister, compacted bentonite, tunnel backfill and surrounding bedrock [1]. Furthermore, the low solubility of spent nuclear fuel can also be considered as a transport barrier. The bedrock is a natural barrier that secures stable and predictable chemical, hydraulic and mechanical conditions which are used as a basis for the technical design of other barriers, and the performance assessment of the repository system for the required period of time [2]. If the radionuclides are released into the bedrock and groundwater, they will be transported mainly by advection along water conducting fractures [3]. The transport of the radionuclides will be retarded by molecular diffusion from the fractures into the stagnant pore water and by sorption onto mineral surfaces in the rock matrix [4, 5, 6]. To these ends, the transport properties of the bedrock (i.e. porosity, effective diffusion coefficient and distribution coefficient) have to be carefully determined for the safety assessment of the final disposal.

Typically, the transport properties of the rock are determined using well controlled laboratory experiments. In the simplest case, these experiments have been performed using through diffusion experiments where fluxes of radionuclides through the drill core samples are measured and the transport properties are determined from the breakthrough curves [7, 8, 9, 10]. Slightly advanced measurements include advection in a fracture coupled with matrix diffusion [11, 6, 12] or even with sorption Hölttä et al. [13], Tachi et al. [14]. These experiments aim to demonstrate the retarding effects of matrix diffusion and sorption in cases comparable with groundwater flow in fractured rock. It has been shown that even in well controlled laboratory experiments the advection field may be challenging to resolve and that properties of the fractures affect heavily to the measured breakthrough curves [15, 16]. Hence, it is beneficial to simplify the flow channel in order to reliably determine the transport properties of the bedrock.

The distribution coefficients of radionuclides have often been determined using batch sorption experiments on crushed rock. However, recent studies

show that the distribution coefficients determined using such experiments overestimate the sorption capacity of the rock due to increased specific surface area [17, 18, 19, 20]. Alternative ways for measuring the distribution coefficients using intact rock has been suggested in these studies and their results show that the results of batch sorption are typically about one order of magnitude larger than the ones determined for intact rock samples.

Recently, increasing interest has arisen to perform in-situ experiments in order to determine the transport properties under realistic conditions for the safety assessment. The in-situ transport experiments have been performed in several countries e.g. Finland [21, 22], Sweden [23, 24], Switzerland [25, 26, 27] and Canada [28] to study the behavior of radionuclides in crystalline bedrock. The in-situ experiments provide important parameters and information for the safety assessment. However, the boundary conditions of in-situ experiments are difficult to control due to in-situ pressure fields and thus the experiments need to be carefully designed. Furthermore, in some occasions it has been proven to be challenging to interpret the results of in-situ experiments and to obtain relevant information for the safety assessment [29, 30]. The in-situ experiments, in general, demand more designing, time and financial resources than the laboratory experiments and thus supporting laboratory experiments are needed. To these ends, it is important to perform the laboratory and in-situ experiments in exactly the same rock using similar experimental design.

This study is a part of a rock matrix REtention PROperties (REPRO) - project being performed at ONKALO, the underground rock characterization facility in Olkiluoto, Finland. The project consists of extensive series of in-situ sorption and diffusion experiments that are supplemented by laboratory studies [31, 32]. The aim of the REPRO-project is to quantify the distribution coefficients, effective diffusion coefficients and connected porosity of the unaltered rock matrix in the repository level stress conditions. The in-situ experiments are performed in drill holes [21, 22] while the drill cores from the same sections are used in laboratory experiments [33, 34, 12, 35, 36, 37, 38, 20, 39]. The supporting laboratory program provides data that can be used to assess the differences caused by the experimental conditions or cannot be determined in-situ (e.g. mineralogy and pore structure [37]).

In this study, Water Phase Diffusion Experiments (WPDE) in laboratory and in-situ conditions has been to performed using the equivalent rock in both of the experiments. Experimental setups include an annular flow channel that is in contact with the rock matrix. The aim has been to study the

interaction of radionuclides that are transported by advection in the channel and determine transport parameters from the measured breakthrough curves. The in-situ experiment provides data on transport properties under realistic conditions for the safety assessment. Furthermore, the comparison of the results from the laboratory and in-situ experiments provides information if the different conditions affect the transport parameters.

2. Materials and Methods

2.1. Rock samples and description of the experimental site

The Olkiluoto island is located on the coast of south-western Finland. The experimental site of REPRO project is located at main characterization level (420 meters below the surface) in ONKALO, underground rock characterization facility. The REPRO experiments are focused mainly on the characterization of veined gneiss (VGN) which is the most abundant rock type (43 %) in the Olkiluoto bedrock according to drill core analyses [40]. Veined gneisses are a subgroup of migmatitic gneisses and they contain diverse elongated, folded or stretched leucosomes with diameter from several millimetres up to ten centimetres [40]. The main minerals of VGN are quartz, plagioclase, biotite and potassium feldspar. Cordierite, muscovite, chlorite and sillimanite are also found as minor components in VGN samples from REPRO site [37]. The mineral composition of the bedrock has been shown to be an important factor for the overall sorption properties of the rock [41, 42, 43, 19].

In the laboratory experiments of the REPRO project, pegmatitic granite (PGR) has also been used [33, 38]. The proportion of PGR in the bedrock of Olkiluoto island is about 20 % according to drill core analyses [40]. The pegmatitic granites are typically leucocratic, allotriomorphic-granular and very coarse-grained, granitic rocks. PGR resembles the leucosome veins in VGN which is the main rock type of the in-situ WPDE and thus it is important to study PGR in the laboratory conditions. The mineralogical studies performed for REPRO samples show that the most abundant mineral in PGR is quartz, with potassium feldspar and plagioclase as other main minerals [37]. Muscovite and garnet were also found as minor components.

The in-situ WPDE was performed in drill hole ONK-PP323. The experimental section ranged from 17.95 m to 19.85 m and it contained VGN with about 10 % of leucosome veins. The laboratory WPDE were performed using two different drill core samples. The first one was collected from the

109 section of in-situ WPDE ranging from 19.25 m to 20.05 m. The foliation of
 110 VGN was roughly perpendicular to the main axis of the drill core and hole
 111 [33]. In both of the experiments, the main direction of diffusion is along
 112 the foliation due to direction of it and thus it can be considered that the
 113 foliation cannot cause difference between the results from in-situ and labora-
 114 tory experiments. The second sample consisted of PGR and it was collected
 115 from drill core ONK-PP318 ranging from 11.98 m to 12.78 m. Previously,
 116 the laboratory samples were used in gas phase matrix diffusion experiments
 117 [12]. Before the laboratory WPDE the samples were equilibrated in syn-
 118 thetic REPRO groundwater [22] for two months. Similar water was used in
 119 the in-situ WPDE. The composition of the synthetic groundwater has been
 120 prepared according to the groundwater collected near REPRO site.

121 *2.2. Water phase diffusion experiments (WPDE)*

122 The basic idea of the laboratory and in-situ WPDE is to inject a short
 123 pulse of tracer solution into a flow channel that is in contact with the rock
 124 matrix. During the experiment, the pulse is transported in the flow channel
 125 and the radionuclides interact with the rock matrix. The transport param-
 126 eters of the rock can be determined from the measured breakthrough curves.
 127 The experimental setups consist of a pump, injection system, annular flow
 128 channel and sample collection system. The annular flow channels are formed
 129 by: 1. The wall of the drill hole and impermeable dummy inside the drill
 130 hole in the in-situ WPDE1 and WPDE2. the surface of the drill core and a
 131 plastic tube around the drill core in the laboratory WPDE (see Fig. 1). The
 132 only difference in the basic idea is that in the laboratory experiment the main
 133 direction of the diffusion inward into the drill core sample while in the in-situ
 134 WPDE the main direction is outward from the flow channel. In principle,
 135 the experimental system mimics groundwater flow in fractured crystalline
 136 rock. However, the structure of the fracture is simplified so that the trans-
 137 port properties of the rock matrix can be determined from the breakthrough
 138 curves.

139 During testing of the experimental setup using uranine in laboratory
 140 setup, it was seen that the water flow was channeled even though inlet and
 141 outlet systems were carefully designed [44]. The mathematical models con-
 142 structed below in Secs. 2.3.1 and 2.3.2 contain a flow channel that is divided
 143 into flowing and stagnant sectors due to the observed heterogeneous flow field
 144 (see Fig. 1).

Figure 1: Schematics of the in-situ (left) and laboratory (right) WPDE diffusion showing transport directions of radionuclides by advection (red) and diffusion through interfaces (orange). The annular flow channels consist of flowing (dark blue) and stagnant (light blue) water.

2.2.1. Laboratory water phase diffusion experiment

The laboratory WPDE's were performed using VGN and PGR drill core samples with a length of 80 cm. In the experiments, a 2 mm thick annular flow channel was created between a plastic tube (inner diameter 46 mm) and the drill core sample (outer diameter 42 mm) (see Fig. 2). The sample was placed in the center of the tube using three curved triangular spacers. The flow of synthetic REPRO groundwater [22] was generated through the flow channel with a constant flow rate of $20 \mu\text{l}/\text{min}$. The water flow was conducted into the annular flow channel via PEEK capillary tube (inner diameter 0.51 mm). An inlet and outlet of the flow channel were constructed into the ends of the drill core samples using three triangular spacers. The spacers divided the flow into three identical flow paths which were connected into a single annular channel using the curved spacers. The tracer pulse, containing HTO and ^{36}Cl , was injected into the flow in the beginning of the experiment using an injection valve (9725i, Rheodyne) that contained a injection loop with a volume of 0.5 ml. Previously, [34] performed successfully similar experiments for unsaturated samples in gas phase and [45] have reported preliminary results for the measurement performed for VGN sample.

The flow was generated using a peristaltic pump (IP 4, Ismatec) and the flow rate was measured continuously with a precision scale (At400, Mettler Toledo). Water samples were collected from the outlet using a fraction collector (Retriever 500, Teledyne ISCO) with a collection time of 4 h and

Figure 2: The experimental setup of the laboratory WPDE consisted of a peristaltic pump, injection system of radionuclides, annular flow channel between a plastic tube and drill core sample and fraction collector.

sample volume of 4.8 ml. the sample vials contained about 0.3 ml of paraffin oil to prevent evaporation during sample collection. Concentrations of HTO and ^{36}Cl as a function of time, i.e. the breakthrough curves, were measured from the collected water samples with a liquid scintillation counter (Tri-Carb 2910 TR, PerkinElmer). The activities were determined using a background subtraction, double labelling and manual quench correction.

2.2.2. In-situ water phase diffusion experiment

Two in-situ WPDE's were performed with flow rates of $20\ \mu\text{l}/\text{min}$ (WPDE1) and $10\ \mu\text{l}/\text{min}$ (WPDE2). In the in-situ experiments, a 1.25 mm thick and 1.9 m long annular flow channel was created between the drill hole surface (inner diameter 56.5 mm) drill hole and an impermeable PEEK (PolyEtherEtherKetone) dummy (outer diameter 54 mm) (see Figs. 1 and 3). Synthetic REPRO groundwater was pumped continuously through the flow channel with two different flow rates. The flow was generated by a high-precision piston pump and the flow rate was determined from the position of the piston of the pump [21, 46]. At the beginning of the experiments, a concentrated tracer pulses of 1 ml and 3 ml for WPDE1 and WPDE2, respectively, were injected. The injected tracer solution in WPDE1 comprised the radioisotopes HTO, ^{22}Na , ^{36}Cl and ^{125}I , of which ^{22}Na was expected to be slightly sorbing. In WPDE2, ^{125}I was excluded and ^{85}Sr and ^{133}Ba (divalent cations with more sorbing properties than ^{22}Na , ($K_d(^{22}\text{Na}) < K_d(^{85}\text{Sr}) < K_d(^{133}\text{Ba})$) were incorporated. However, focus is this work is in the comparison of the results and thus only results for HTO, ^{22}Na and ^{36}Cl are presented. The experimental section was isolated by borehole packers and pressure in the system

191 (about 2.2 MPa) was maintained and regulated to be slightly lower (4-8 kPa)
 192 than the surrounding pressure to avoid the advection of radionuclides into
 193 the rock. The technical construction of the experiments is presented in more
 194 details by [21, 46].

Figure 3: The experimental setup of the in-situ WPDE consisted of a high-precision piston pump, injection and sampling valve of radionuclides and annular flow channel between a drill hole and impermeable dummy. The experimental system was isolated from the rest of the drill hole using packers.

195 The breakthrough curves were determined by collecting groundwater sam-
 196 ples with a volume of 0.5 ml from the out flowing water using a six-way valve
 197 (see Fig 3). Collected samples were first measured with a HPGe gamma spec-
 198 trometer (either Canberra GX8021-7500SL Xtra with 80% relative efficiency
 199 or Canberra GC4519 with 45% relative efficiency) for the activities of all
 200 gamma-emitting nuclides (^{22}Na , ^{85}Sr , ^{125}I and ^{133}Ba). This was followed by
 201 a separation of pure beta-emitter ^{36}Cl by silver chloride precipitation. The
 202 precipitate was dissolved in strong ammonia, mixed with liquid scintillation
 203 cocktail (Ultima GoldTM AB, PerkinElmer) and measured by liquid scintilla-
 204 tion counting (TriCarb 2910TR, PerkinElmer). The supernatant containing
 205 the fraction of other pure beta emitter HTO was measured similarly with
 206 liquid scintillation counting. Of the gamma emitters, ^{22}Na and ^{85}Sr were
 207 well separated from the supertantant but part of the ^{125}I and ^{133}Ba ended up
 208 both in the precipitate and the supernatant. This needed to be taken into
 209 account when calculating the results since these gamma emitters have ma-
 210 jor beta/electron emissions. The chemical separations and spectral analyses
 211 have been presented and discussed in more details by Qian et al. [47]. Fur-
 212 thermore, the breakthrough of gamma-emitting nuclides (^{22}Na , ^{85}Sr , ^{125}I and

213 ^{133}Ba) were followed on-line using Na(Tl)I-scintillation detector (digiBASE,
214 Ortec) inside the experiment container located in the REPRO site.

215 2.3. Mathematical model

216 The measured breakthrough curves from the laboratory and in-situ WPDE
217 were modelled using analytic solutions of advection-diffusion-equation in
218 cylindrical coordinates. The illustration of constructed models are shown
219 in Fig. 1.

220 2.3.1. Laboratory experiment

221 First, the transport of a soluble tracer in fluid flow through a channel
222 with an annular cross section surrounding a cylinder of porous medium is
223 considered. Tracer concentration in the flow channel (C) can be described
224 with the equation

$$\frac{\partial C}{\partial t} + \nabla \cdot (C v) - D \Delta C = 0, \quad (1)$$

225 where v is the velocity of the flow, and D is the diffusion coefficient of the
226 tracer in the fluid. In the porous matrix the concentration of the tracer in the
227 water phase (C_m) and sorbed on the rock matrix (C_r) can now be described
228 with the equation

$$\epsilon_p \frac{\partial C_m}{\partial t} + (1 - \epsilon_p) \rho_r \frac{\partial C_r}{\partial t} - \nabla \cdot (\epsilon_p D_p \nabla C_m) = 0, \quad (2)$$

229 where D_p is the pore diffusion coefficient of the tracer in the matrix, ϵ_p is
230 the porosity and ρ_r the density of the rock. Assume that the rock matrix
231 is homogeneous and the sorption is governed by a linear equilibrium isotherm
232 and an instantaneous equilibrium between solid and liquid phases. So

$$C_r = K_d C_m, \quad (3)$$

233 where K_d is a linear equilibrium sorption constant and the equation (2) leads
234 to a diffusion equation

$$\frac{\partial C_m}{\partial t} - D_a \Delta C_m = 0, \quad (4)$$

235 where D_a is the apparent diffusion coefficient

$$D_a = \frac{\epsilon_p D_p}{\epsilon_p + (1 - \epsilon_p) \rho_r K_d}. \quad (5)$$

236 At the outer wall of the flow channel, the normal derivative of C vanishes

$$\frac{\partial C}{\partial n} = 0, \quad (6)$$

237 and the boundary condition between the channel and the porous matrix is

$$C = C_m, \quad \text{and} \quad D \frac{\partial C}{\partial n} = \epsilon_p D_p \frac{\partial C_m}{\partial n}. \quad (7)$$

238 When using experimental setup described in Sec. 2.2, it can be assumed
 239 that the velocity v is parallel to the axis of the cylinder (x -direction) and
 240 that the velocity profile does not depend on x . It can also be assumed that
 241 the flow is well mixed in the radial direction and thus a radial average of the
 242 concentration over the flow channel can be taken and we get

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} - D_{eff} \frac{\partial^2 C}{\partial x^2} - \frac{2 D \log(1 + \frac{b}{a})}{2ab + b^2} \cdot \frac{\partial^2 C}{\partial \phi^2} = - \frac{2\epsilon_p D_p a}{2ab + b^2} \frac{\partial C_m}{\partial r} \Big|_{r=a}. \quad (8)$$

243 Here C is now the radial average of the tracer concentration and v is a
 244 radial average of the velocity, a is the inner radius and b the aperture of the
 245 flow channel. Diffusion coefficient D is replaced with the effective diffusion
 246 coefficient D_{eff} which takes into account the Taylorian dispersion Kekäläinen
 247 et al. [6].

248 As in the preliminary test it was noticed that the flow was channelled (see
 249 Sec. 2.2), the flow channel is divided into flowing part (velocity v in sector
 250 $-\phi_0 \leq \phi \leq \phi_0$) and stagnant part (velocity 0 elsewhere). Furthermore, it
 251 is assumed that at the beginning of the experiment there is no tracer in the
 252 system and a short pulse of the tracer is injected into the flow channel. Since
 253 advection in the flowing part of the channel is much faster than transport
 254 by diffusion in the stagnant part, the longitudinal component of the concen-
 255 tration gradient in the stagnant part is very small in comparison with the
 256 angular one. Thus it is assumed that the diffusion in the stagnant part of
 257 the flow channel is purely angular. For similar reason it can be assumed that
 258 the diffusion in the rock matrix is radial. When taking an angular average of
 259 the tracer concentration over the flowing sector of the channel and assume a

260 well-mixed flow, the following equations describe the system:

$$\begin{aligned}
& \frac{\partial C_f}{\partial t} + v \frac{\partial C_f}{\partial x} - D_{eff} \frac{\partial^2 C_f}{\partial x^2} \\
& = -\frac{2\epsilon_p D_p a}{2ab + b^2} \left. \frac{\partial C_m^{(f)}}{\partial r} \right|_{r=a} + \frac{2D \log(1 + \frac{b}{a})}{\phi_0(2ab + b^2)} \cdot \left. \frac{\partial C_s}{\partial \phi} \right|_{\phi=\phi_0}, \quad (9) \\
& \frac{\partial C_s}{\partial t} - \frac{2D \log(1 + \frac{b}{a})}{2ab + b^2} \cdot \frac{\partial^2 C_s}{\partial \phi^2} = -\frac{2\epsilon_p D_p a}{2ab + b^2} \left. \frac{\partial C_m^{(s)}}{\partial r} \right|_{r=a}.
\end{aligned}$$

261 Here C_f is the (average) concentration of the tracer in the flowing sector of
 262 the channel and C_s is the concentration in the stagnant part of the channel
 263 ($\phi_0 \leq \phi \leq 2\pi - \phi_0$). $C_m^{(f)}$ and $C_m^{(s)}$ are the concentrations in the corresponding
 264 sectors in the rock matrix. In the rock matrix, diffusion is radial

$$\frac{\partial C_m}{\partial t} - D_a \left(\frac{\partial^2 C_m}{\partial r^2} + \frac{1}{r} \frac{\partial C_m}{\partial r} \right) = 0, \quad (r < a) \quad (10)$$

265 and the concentrations are continuous:

$$C_m^{(f)}|_{r=a} = C_f, \quad C_m^{(s)}|_{r=a} = C_s, \quad C_s|_{\phi=\phi_0} = C_s|_{\phi=2\pi-\phi_0} = C_f. \quad (11)$$

266 In the beginning of the experiment ($t = 0$) a short pulse of tracer (total
 267 activity A_0) is injected into the inlet ($x = 0$) of the channel. The boundary
 268 condition for concentration at the inlet ($C_f(0, t)$) can be described by Dirac
 269 delta function

$$C_f(0, t) = \frac{A_0}{\phi_0(2ab + b^2)v} \delta(t). \quad (12)$$

270 In the measurements, breakthrough curves are measured i.e. the concentra-
 271 tion at the outlet $C_f(L, t)$ (L is the length of the channel). A boundary
 272 condition for the outlet is not set. However, we consider an unbounded sys-
 273 tem ($x > 0$) with a physical boundary condition at infinity

$$\lim_{x \rightarrow \infty} C_f(x, t) = 0. \quad (13)$$

274 2.3.2. In-situ -experiment

275 In the case of in-situ WPDE, the setup is geometrically similar but the
 276 flow channel is surrounded by a porous matrix. The system can be described
 277 with the same Eqs. (1) – (11) but the zero flux boundary condition is on

the inner wall of the flow channel. After making the same assumptions as in the case of laboratory WPDE, following equations describing the system are obtained:

$$\begin{aligned} \frac{\partial C_f}{\partial t} + v \frac{\partial C_f}{\partial x} - D_{eff} \frac{\partial^2 C_f}{\partial x^2} \\ = \frac{2\epsilon_p D_p a}{2ab - b^2} \left. \frac{\partial C_m^{(f)}}{\partial r} \right|_{r=a} + \frac{2 D \log(\frac{a}{a-b})}{\phi_0(2ab - b^2)} \cdot \left. \frac{\partial C_s}{\partial \phi} \right|_{\phi=\phi_0}, \quad (14) \\ \frac{\partial C_s}{\partial t} - \frac{2 D \log(\frac{a}{a-b})}{2ab - b^2} \cdot \frac{\partial^2 C_s}{\partial \phi^2} = \frac{2\epsilon_p D_p a}{2ab - b^2} \left. \frac{\partial C_m^{(s)}}{\partial r} \right|_{r=a}. \end{aligned}$$

In this case, the parameter a is the outer radius of the flow channel, and the diffusion in the matrix is outwards

$$\frac{\partial C_m}{\partial t} - D_a \left(\frac{\partial^2 C_m}{\partial r^2} + \frac{1}{r} \frac{\partial C_m}{\partial r} \right) = 0, \quad (r > a). \quad (15)$$

We have the same boundary conditions Eq. (11), and zero initial condition as in the previous case. However, a bounded matrix ($a < r < R$) and a zero flux at the boundary $r = R$ are considered. The boundary R is set far from the flow channel so that the effect of it on the breakthrough curve is negligible in the time scale of the experiment. In this case, the concentration in the inlet takes a form

$$C_f(0, t) = \frac{A_0}{\phi_0(2ab - b^2)v} \delta(t). \quad (16)$$

2.3.3. The solution of the model

In the laboratory and in-situ WPDE, the breakthrough curves $C_f(L, t)$ are measured. The solutions of the constructed models are shown in the Appendix A. It turns out that the solution for the breakthrough curve can be expressed in the form of an integral

$$C_f(L, t) = C_0 \frac{\sqrt{2}}{\pi} \int_0^\infty e^{-G(x) - \tau x} \sin\left(\frac{\pi}{4} + H(x) - \tau x\right) dx, \quad (17)$$

where $\tau = \frac{tv}{L}$. The details of Eq. (17) and expressions for $G(x)$ and $H(x)$ for the laboratory and in-situ WPDE can be found in the Appendix A.

3. Results

3.1. laboratory WPDE - inward diffusion

The laboratory WPDE's were performed for VGN and PGR samples using HTO and ^{36}Cl as tracers. The measured and modelled breakthrough curves are shown in Fig. 4. The early part ($t \lesssim 2000\text{ h}$) of the breakthrough curve was dominated by advective transport and the retarding effect of matrix diffusion was seen as a strong tailing of the late part of the curve ($t \gtrsim 2000\text{ h}$). Furthermore, the early part of the breakthrough curve is affected by the channelled flow field. It was not possible to model the breakthrough curves using a model with constant flow velocity. The first breakthrough ($t \lesssim 100\text{ h}$) occurred earlier and the advective part of the curve was wider than it was predicted by such model. Previously it has been shown that the flow field was channelled in pretests [44] and thus it was justified to apply the model presented in Sec. 2.2.1. The fitting was done by first setting the first breakthrough time of the breakthrough curve by adjusting the size of the flowing sector (ϕ_0) and then by setting the late part of the breakthrough curve by adjusting porosity and pore diffusion coefficient. An excellent agreement between measured and modelled breakthrough curves were found using the three fitting parameters. Furthermore, it can be noted that the early part of the breakthrough curve could be modeled by adjusting only the first breakthrough and using the known values for the aperture and length of the flow channel, diameter of the sample, flow rate, and diffusion coefficient of the tracers in water. This increases the reliability of the constructed model and that it takes into account the relevant processes in the system. In both measurements, the early part of the breakthrough curves were identical for both of the tracers. However, measurement performed in VGN showed higher late part of the breakthrough curve for HTO than for ^{36}Cl . This indicates that transport of ^{36}Cl is retarded less by the rock matrix than the transport of HTO. In measurement performed for PGR, this effect was not observed.

The results of the modelling for porosity and pore diffusion coefficient are shown in Table 1. The effective diffusion coefficients were determined using expression $D_e = \epsilon_p \times D_p$. Furthermore, the effective diffusion coefficients were converted to 10°C and parameter αD_e was determined to compare the results with the ones from in-situ WPDE (see Sec. 4). The parameter

$$\alpha = \epsilon_p + (1 - \epsilon_p)\rho K_d \quad (18)$$

Figure 4: The measured (markers) and modelled (solid lines) breakthrough curves of laboratory WPDE performed for VGN (left) and PGR (right) using HTO (green) and ^{36}Cl (blue) as tracers.

is a capacity parameter. The conversion of effective diffusion coefficients was done using the diffusion coefficients of HTO and ^{36}Cl in water at temperatures of $10\text{ }^{\circ}\text{C}$ and $25\text{ }^{\circ}\text{C}$ [48, 49, 50]. The porosity and diffusion coefficients determined from the breakthrough curves of HTO for VGN are significantly larger than the values determined from the breakthrough curves of ^{36}Cl . This was seen as difference in late time behaviour of the breakthrough curves (see Fig. 4. For PGR, the late time behaviour of HTO and ^{36}Cl was identical and thus there is no difference in the determined porosity nor diffusion coefficients.

3.2. *in situ* WPDE - outward diffusion

The in-situ WPDE's were performed in VGN using flow rates of $20\text{ }\mu\text{l}/\text{min}$ (WPDE1) and $10\text{ }\mu\text{l}/\text{min}$ (WPDE2) and HTO, ^{36}Cl and ^{22}Na as tracers. The measured and modelled breakthrough curves are shown in Fig. 5. The shapes of the curves are similar to laboratory experiments shown in Fig. 4. The breakthrough curves consist of the advection dominated early part (WPDE1: $t \lesssim 1000\text{ h}$, WPDE2: $t \lesssim 2500\text{ h}$) and late part (WPDE1: $t \gtrsim 1000\text{ h}$, WPDE2: $t \gtrsim 2500\text{ h}$) that is affected by the rock matrix. Also in the in-situ experiments the first breakthrough occurred earlier than predicted

Table 1: The results for the VGN and PGR samples from the laboratory WPDE from the breakthrough curves of HTO and ^{36}Cl for pore diffusion coefficient (D_p), porosity (ϵ_p), effective diffusion coefficient (D_e) at 25 °C and 10 °C. Furthermore, value for parameter $\alpha D_e = (\epsilon_p + (1 - \epsilon_p)\rho K_d) \times D_e$ is given to comparison with in-situ WPDE results.

Sample	VGN (WPDElab6)	PGR (WPDElab7)
HTO	D_p (m^2/s)	1.4×10^{-11}
	ϵ_p (-)	0.0099
	D_e (25 °C) (m^2/s)	3.6×10^{-14}
	D_e (10 °C) (m^2/s)	2.4×10^{-14}
	αD_e (10 °C) (m^2/s)	7.3×10^{-17}
^{36}Cl	D_p (m^2/s)	1.2×10^{-11}
	ϵ_p (-)	0.0027
	D_e (25 °C) (m^2/s)	3.6×10^{-14}
	D_e (10 °C) (m^2/s)	2.3×10^{-14}
	αD_e (10 °C) (m^2/s)	7.0×10^{-17}

by the model with the non-channeled flow field and thus the model with the
channeled flow field was used for the analyses (see Sec. 2.3.2). Unfortunately
in the in-situ WPDE, the late part of the curve is controlled by parameter
 αD_e due to the additional boundary condition for bounding the matrix (see
Sec. 2.3.2). Hence, the transport parameters of the rock matrix are coupled
and they cannot be determined directly from the breakthrough curves. In
addition, the breakthrough curves of both experiments show that transport
of ^{36}Cl is retarded less and ^{22}Na is retarded more by the rock matrix than
the transport of HTO.

An analysis shown in Fig. 6 was performed due to the coupling of the
transport parameter. In the analysis, the values from the laboratory exper-
iments and Archie's law [51] with case dependent parameters were applied.
First, porosities (non-sorbing nuclides) were plotted as a function of the effec-
tive diffusion coefficient so that parameter αD_e remains constant (see Tables
1 and 2). These plots form linear regions that represent all the possible
realizations that can explain the measured breakthrough curves. This was
followed by connecting the points from laboratory WPDE for HTO and ^{36}Cl
using Archie's law

$$D_e = 0.45 \times \epsilon_p^{1.92} D_w \quad (19)$$

where values from $1.3 \times 10^{-9} m^2/s$ to $1.5 \times 10^{-9} m^2/s$ were used for the
diffusion coefficient of the tracer in water. These values correspond to values

Figure 5: The measured (markers) and modelled (solid lines) breakthrough curves from in-situ WPDE1 (left) and WPDE2 (right) performed using HTO (green), ^{36}Cl (blue) and ^{22}Na (red) as tracers.

of ^{36}Cl and HTO in 10°C , respectively (see Sec. 2.2.1). As the pore space of the sample can be considered similar and the in-situ conditions can affect it only slightly, due to example higher pressure, the Eq. 19 was used to extract information about the porosity and effective diffusion coefficients. The in-situ values for porosities and effective diffusion coefficients were determined from the intersections of Eq. 19 and possible values determined in the first step.

For the analysis of ^{22}Na , the porosity and effective diffusion coefficient from the analysis of HTO were used to estimate the in-situ distribution coefficient distribution coefficient (see Fig. 6). This was performed by using first the effective diffusion coefficient to determine a correct region among the possible combinations and then determining the distribution coefficient at the intersection using the porosity determined from the breakthrough curves of HTO. These analyses enable a comparison of retention parameters from the laboratory and in-situ WPDE.

The numerical results from these analyses are shown in Table 2. First of all the coupled parameter (αD_e) are similar for both of the in-situ experiments. This builds confidence on the model used in the analysis. Small variations in the flowing and stagnant sectors of the flow channel can cause

Figure 6: The retention parameters for in-situ WPDE were analyzed using the parameter αD_e , Archie's law (light gray region) and information from laboratory WPDE (dashed lines) for HTO (green) and ^{36}Cl (blue). The possible values for in-situ parameters are shown as colored areas for HTO (light green), ^{36}Cl (light blue) and ^{22}Na (light red). The in-situ parameters of HTO were applied when extracting information about K_d of ^{22}Na (dashed red lines).

387 such small variations. In both experiments, the transport of ^{36}Cl is retarded
388 less and ^{22}Na is retarded more by the rock matrix than the transport of
389 HTO. This can be seen in the effective diffusion coefficients and in values for
390 coupled parameter (αD_e).

Table 2: The results from in-situ WPDE1 and WPDE2 for (αD_e), porosity (ϵ_p), effective diffusion coefficient (D_e) and distribution coefficient (K_d) determined from the breakthrough curves of HTO, ^{36}Cl and ^{22}Na). Here the laboratory data has been applied to get results for ϵ_p , D_e and K_d (see Fig. 6).

Nuclide	Parameter	WPDE1	WPDE2
HTO	αD_e (m^2/s)	5.4×10^{-16}	2.3×10^{-16}
	ϵ_p (-)	0.0082	0.0061
	D_e (m^2/s)	6.6×10^{-14}	3.8×10^{-14}
^{36}Cl	αD_e (m^2/s)	1.2×10^{-17}	1.3×10^{-17}
	ϵ_p (-)	0.0024	0.0023
	D_e (m^2/s)	5.4×10^{-15}	5.2×10^{-15}
^{22}Na	αD_e (m^2/s)	8.7×10^{-15}	3.8×10^{-15}
	ϵ_p (-)	0.0082	0.0061
	D_e (m^2/s)	6.6×10^{-14}	3.8×10^{-14}
	K_d (m^3/kg)	4.6×10^{-5}	3.5×10^{-5}

391 4. Discussion

392 It was shown that the WPDE experiments can be performed in labo-
393 ratory and in-situ conditions. Similar experimental design of experiments
394 reduces the effects arising from the experimental details that might be sig-
395 nificant if the experimental design would differ. Furthermore, the transport
396 parameters are averaged over relatively large rock volume due the experi-
397 mental design. Hence, the experimental design is relatively insensitive to
398 small heterogeneities in respect to often used through diffusion experiments.
399 Furthermore, the through diffusion experiments are difficult to perform in
400 the in-situ conditions due the pressure gradients that are unknown and im-
401 possible to control. The in-situ experiments performed using different flow
402 rates provided similar results that indicates that the constructed model is
403 able to take into account the relevant processes that affect the breakthrough
404 curves. These facts increase the reliability of the constructed model and the
405 comparison of the results.

406 In general, the porosities and diffusion coefficients determined from the
407 breakthrough curves of HTO and ^{36}Cl (see Tables 1 and 2) are in fair agree-
408 ment with previously determined values for REPRO samples [33, 34, 37, 38]
409 and Olkiluoto samples [9]. However, the variation of previously determined
410 values is relatively large e.g. due to the heterogeneity of the rock, variations
411 between different locations and differences in alteration states of the rock
412 samples.

413 The porosities from the in-situ WPDE are from 12 % to 38 % smaller
414 than the porosities from the laboratory WPDE. Furthermore, the effective
415 diffusion coefficients are from 30 % to 60 % smaller than the coefficients from
416 laboratory experiments. Most probably, the differences arise from the release
417 of the in-situ rock pressure that causes a slight increase of pore apertures and
418 thus an increase of porosity and effective diffusion coefficients. The same ef-
419 fect is seen when comparing the values of αD_e . The values from the in-situ
420 WPDE are about 35 % to 43 % smaller than the parameters from the labo-
421 ratory WPDE. It can be seen that the collecting of the laboratory samples
422 affects slightly the transport parameters of the rock. Due to the conservative
423 nature performance assessment of the spent nuclear fuel repositories, the dif-
424 ference is not very significant. However, the influence needs to be carefully
425 estimated before further conclusions are made.

426 In the laboratory and in-situ WPDE, a considerable difference between
427 the retention parameters of HTO and ^{36}Cl was found. For the VGN, the
428 porosities and effective coefficients determined from the breakthrough curves
429 of ^{36}Cl were found to be considerable smaller than from the breakthrough
430 curves of HTO. This indicates that the transport of ^{36}Cl is retarded less by
431 the rock matrix than the transport of HTO. This finding is consistent with
432 the anion exclusion phenomenon that is caused by an electrical repulsion of
433 anions in the vicinity of negatively charged mineral surfaces in micro-pores
434 ($d < 2 \text{ nm}$) and meso-pores ($2 \text{ nm} < d < 50 \text{ nm}$) [52]. The whole pore space
435 is not accessible for anions due to the repulsion and this can be seen in the
436 comparison of results for HTO and ^{36}Cl . As the anion exclusion limits the
437 available pore space for ^{36}Cl ions and may even prevent their transport in
438 nanometer scale pores, the effective diffusion coefficient of ^{36}Cl is also lower
439 than of HTO. The porosities determined from the breakthrough curves of ^{36}Cl
440 cannot be considered as true physical porosities but as chloride accessible
441 porosities or effective porosities as e.g. Smith et al. [53] have defined it.
442 In general, the mechanism of anion exclusion is well known and it is
443 routinely modeled in the framework of theories describing the properties of

444 the electrical double layer [54]. The effect of anion exclusion, however, has
445 been observed mostly in clay rocks [55, 56, 57] whereas the effect has been
446 observed in limited number of crystalline rock samples [9, 10, 35]. In VGN,
447 the effect of anion exclusion is large enough to explain the imbalance of
448 chloride content measured between fracture and matrix pore water due to
449 reduced chloride accessible porosity and diffusivity [9].

450 In the laboratory WPDE for PGR, the effect of anion exclusion was not
451 observed. In previous studies by Sammaljärvi et al. [37] and Voutilainen
452 et al. [58], it has been shown that VGN and PGR samples from REPRO
453 site differ considerably with respect to pore space and mica and clay mineral
454 content. In VGN, the pore space consists mostly of inter-lamellar pores in
455 mica minerals (biotite, muscovite and chlorite). The apertures of the inter-
456 lamellar are within a few nanometer meters. Furthermore, some cleavages
457 between biotite lamellae were clay minerals that are known to cause anion
458 exclusion [37]. Presence of micro- and meso-pores in such minerals can reduce
459 available pore space of chloride and cause the observed difference in transport
460 parameters of HTO and ^{36}Cl for VGN. On the other hand, the pore space of
461 PGR consists mainly of inter- and trans-granular fissures and grain boundary
462 pores that are typically from $1\text{ }\mu\text{m}$ to $30\text{ }\mu\text{m}$ [37]. The electrical double layer
463 is small (max 4 nm) in comparison with the aperture of these pores and
464 fissures and thus its effect on chloride accessible porosity is negligible. On
465 that account, the effect of anion exclusion was not observed for PGR. Based
466 on these observations it can be concluded that anion exclusion seems to be
467 linked with the properties of the pore space and abundance of biotite and
468 clay minerals of the sample.

469 Previously, the distribution coefficient of ^{22}Na for VGN was determined
470 in similar conditions except using batch sorption experiments with crushed
471 rock sample [39]. Their result for the distribution coefficient $((2.0 \pm 0.5) \times$
472 $10^{-4}\text{ m}^3/\text{kg})$ was found to be almost one order of magnitude larger than
473 from in-situ WPDE (see Table 2. This can be explained by an increase of
474 specific surface area due to the crushing of the sample. Similar differences
475 have been found previously for distribution coefficients of e.g. cesium, barium
476 and strontium in laboratory experiments [8, 17, 19, 59]. The results of this
477 study support the conclusion of the previous studies that the distribution
478 coefficients of radionuclides used in the safety assessment of the spent nuclear
479 fuel repository should be determined using intact rock when feasible. When
480 applying distribution coefficients determined for crushed rock, conservative
481 estimates for conversion factors should be used [60]. This, on the other hand,

482 may lead to an overestimation of flux of the sorbing radionuclides and thus
483 cause inflation of the risks.

484 5. Conclusions

485 The laboratory and in-situ Water Phase Diffusion Experiments (WPDE)
486 were introduced. The experiments were successfully performed and modeled
487 using the analytical solutions of the constructed mathematical model. It was
488 demonstrated that such experiments are capable to provide reliable data on
489 the transport parameters of intact rock over larger rock volumes than typical
490 through diffusion experiments. The porosity of the rock, effective diffusion
491 coefficients of HTO and ^{36}Cl and distribution coefficient of ^{22}Na for VGN
492 were determined applying the experiments that mimic water flow in a frac-
493 ture and interaction of radionuclides, that are being transported by the flow,
494 with the rock matrix. These parameters are in great importance when as-
495 sessing the ability of bedrock to retard the transport of radionuclides towards
496 biosphere. The porosity and effective diffusion coefficients of HTO and ^{36}Cl
497 were found to be in agreement with previously determined values for REPRO
498 and Olkiluoto samples. However, the porosities and effective diffusion coeffi-
499 cients determined from in-situ WPDE were found to be slightly smaller than
500 the parameters from the laboratory WPDE. Furthermore, the distribution
501 coefficients of ^{22}Na were found to be about one order of magnitude smaller
502 than the coefficients determined previously by batch sorption experiments.
503 These findings indicate that the transport of radionuclides in fracture flow
504 may be retarded less by the rock matrix in the in-situ conditions than the
505 laboratory experiments suggest. The influence on the safety assessment of
506 the repository caused by the observed differences needs to be carefully es-
507 timated. However, the in-situ WPDE provided valuable site specific data
508 in conditions relevant to the repository being built and the results can be
509 readily used in the safety assessment of the repository instead of conservative
510 estimates.

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731 Appendix A. The solution of the model

732 Appendix A.1. Laboratory experiment

733 Let's consider first the model given in Eqs. (9) – (13) for the laboratory
734 WPDE. With the substitution

$$\begin{aligned}
 \tau &= \frac{tv}{L}, & \xi &= \frac{x}{L}, & \rho &= \frac{r}{a}, & \psi &= \frac{\phi - \phi_0}{2\pi - 2\phi_0} \\
 C_1(\xi, \tau) &= \frac{C_f(x, t)}{C_0}, \\
 C_2(\xi, \psi, \tau) &= \frac{C_s(x, \phi, t)}{C_0}, \\
 C_M^{(1)}(\xi, \rho, \tau) &= \frac{C_m^{(f)}(x, r, t)}{C_0} \\
 C_M^{(2)}(\xi, \psi, \rho, \tau) &= \frac{C_m^{(s)}(x, \phi, r, t)}{C_0}
 \end{aligned} \tag{A.1}$$

735 where

$$C_0 = \frac{A_0}{\phi_0(2ab + b^2)L}, \tag{A.2}$$

736 the equations describing the problem can be expressed in a dimensionless
737 form:

$$\begin{aligned}
 &\frac{\partial C_1}{\partial \tau}(\xi, \tau) + \frac{\partial C_1}{\partial \xi}(\xi, \tau) - \mu^2 \frac{\partial^2 C_1}{\partial \xi^2}(\xi, \tau) \\
 &= -\frac{\lambda}{\kappa} \frac{\partial C_M^{(1)}}{\partial \rho}(\xi, 1, \tau) + 2 \frac{\pi - \phi_0}{\phi_0} \mu_s^2 \frac{\partial C_2}{\partial \psi}(\xi, 0, \tau) \\
 &\frac{\partial C_2}{\partial \tau}(\xi, \psi, \tau) - \mu_s^2 \frac{\partial^2 C_2}{\partial \xi^2}(\xi, \psi, \tau) = -\frac{\lambda}{\kappa} \frac{\partial C_M^{(2)}}{\partial \rho}(\xi, \psi, 1, \tau) \\
 &\frac{\partial C_M^{(1)}}{\partial \tau}(\xi, \rho, \tau) - \frac{1}{\kappa^2} \left(\frac{\partial^2 C_M^{(1)}}{\partial \rho^2}(\xi, \rho, \tau) + \frac{1}{\rho} \frac{\partial C_M^{(1)}}{\partial \rho}(\xi, \rho, \tau) \right) = 0 \\
 &\frac{\partial C_M^{(2)}}{\partial \tau}(\xi, \psi, \rho, \tau) - \frac{1}{\kappa^2} \left(\frac{\partial^2 C_M^{(2)}}{\partial \rho^2}(\xi, \psi, \rho, \tau) + \frac{1}{\rho} \frac{\partial C_M^{(2)}}{\partial \rho}(\xi, \psi, \rho, \tau) \right) = 0,
 \end{aligned} \tag{A.3}$$

738 with boundary and initial conditions

$$\begin{aligned}
C_M^{(1)}(\xi, 1, \tau) &= C_1(\xi, \tau), \quad C_M^{(1)}(\xi, \rho, 0) = 0, \\
C_M^{(2)}(\xi, \psi, 1, \tau) &= C_2(\xi, \psi, \tau), \quad C_M^{(2)}(\xi, \psi, \rho, 0) = 0, \\
C_2(\xi, 0, \tau) &= C_2(\xi, 1, \tau) = C_1(\xi, \tau) \\
C_1(0, \tau) &= \delta(\tau), \quad \lim_{\xi \rightarrow \infty} C_1(\xi, \tau) = 0, \quad C_1(\xi, 0) = 0.
\end{aligned} \tag{A.4}$$

739 Here the dimensionless parameters are

$$\begin{aligned}
\lambda &= \frac{2(\epsilon_p + (1 - \epsilon_p)\rho_r K_d)a}{2ab + b^2} \sqrt{\frac{D_a L}{v}}, \quad \kappa = a \sqrt{\frac{v}{D_a L}}, \\
\mu &= \sqrt{\frac{D_{eff}}{Lv}}, \quad \mu_s = \frac{1}{\pi - \phi_0} \sqrt{\frac{D \log(1 + \frac{b}{a}) L}{2v(2ab + b^2)}}.
\end{aligned} \tag{A.5}$$

740 For a fixed ξ and ψ , the diffusion equation for $C_M^{(2)}$ can be solved by separating
741 the variables:

$$C_M^{(2)}(\xi, \psi, \rho, \tau) = C_2(\xi, \psi, \tau) - 2 \sum_{n=1}^{\infty} \frac{J_0(\alpha_n \rho)}{\alpha_n J_1(\alpha_n)} \int_0^{\tau} e^{-\frac{\alpha_n^2}{\kappa^2}(\tau-\sigma)} \frac{\partial C_2}{\partial \sigma}(\xi, \psi, \sigma) d\sigma \tag{A.6}$$

742 where $0 < \alpha_1 < \alpha_2 < \dots$ are the zeroes of the Bessel function J_0 . By
743 substituting this solution in Eq. (A.3) for C_2 , an integro-differential equation
744 for C_2 is obtained:

$$\frac{\partial C_2}{\partial \tau}(\xi, \psi, \tau) - \mu_s^2 \frac{\partial^2 C_2}{\partial \xi^2}(\xi, \psi, \tau) = -\lambda \int_0^{\tau} \Lambda(\tau - \sigma) \frac{\partial C_2}{\partial \sigma}(\xi, \psi, \sigma) d\sigma, \tag{A.7}$$

745 with boundary and initial conditions

$$C_2(\xi, 0, \tau) = C_2(\xi, 1, \tau) = C_1(\xi, \tau), \quad C_2(\xi, \psi, 0) = 0 \tag{A.8}$$

746 where

$$\Lambda(\tau) = \frac{2}{\kappa} \sum_{n=1}^{\infty} e^{-\frac{\alpha_n^2}{\kappa^2} \tau}. \tag{A.9}$$

747 By taking a Laplace transform with respect to the variable τ , following equa-
 748 tion is obtained:

$$\begin{aligned} s \hat{C}_2(\xi, \psi, s) - \mu_s^2 \frac{\partial^2 \hat{C}_2}{\partial \psi^2}(\xi, \psi, s) &= -\lambda \hat{\Lambda}(s) s \hat{C}_2(\xi, \psi, s), \\ \hat{C}_2(\xi, 0, s) &= \hat{C}_2(\xi, 1, s) = \hat{C}_1(\xi, s) \end{aligned} \quad (\text{A.10})$$

749 where the Laplace transform of Λ is

$$\hat{\Lambda}(s) = \frac{2}{\kappa} \sum_{n=1}^{\infty} \frac{1}{s + \frac{\alpha_n^2}{\kappa^2}}. \quad (\text{A.11})$$

750 Now the solution for the Eq. (A.10) can be written in form:

$$\hat{C}_2(\xi, \psi, s) = \hat{C}_1(\xi, s) \cdot \frac{\cosh\left(\frac{\sqrt{s(1+\lambda\hat{\Lambda}(s))}}{\mu_s} \left(\frac{1}{2} - \psi\right)\right)}{\cosh \frac{\sqrt{s(1+\lambda\hat{\Lambda}(s))}}{2\mu_s}}. \quad (\text{A.12})$$

751 Similarly for a fixed ξ , the diffusion equation for $C_M^{(1)}$ can be solved by sepa-
 752 rating the variables:

$$C_M^{(1)}(\xi, \rho, \tau) = C_1(\xi, \tau) - 2 \sum_{n=1}^{\infty} \frac{J_0(\alpha_n \rho)}{\alpha_n J_1(\alpha_n)} \int_0^{\tau} e^{-\frac{\alpha_n^2}{\kappa^2}(\tau-\sigma)} \frac{\partial C_1}{\partial \sigma}(\xi, \sigma) d\sigma. \quad (\text{A.13})$$

753 By substituting this solution in Eq. (A.3) for C_1 , taking the Laplace trans-
 754 form with respect to the variable τ , and using the Eq. (A.12), a differential
 755 equation for the Laplace transform of C_1 is obtained:

$$\begin{aligned} s \hat{C}_1(\xi, s) + \frac{\partial \hat{C}_1}{\partial \xi}(\xi, s) - \mu^2 \frac{\partial^2 \hat{C}_1}{\partial \xi^2}(\xi, s) &= -\lambda s \hat{\Lambda}(s) \hat{C}_1(\xi, s) \\ &\quad - \tilde{\lambda} \hat{C}_1(\xi, s) \sqrt{s(1+\lambda\hat{\Lambda}(s))} \tanh\left(\tilde{\kappa} \sqrt{s(1+\lambda\hat{\Lambda}(s))}\right) \end{aligned} \quad (\text{A.14})$$

756 and the Laplace transformed boundary conditions in Eq. (A.3) for C_1 are

$$\hat{C}_1(0, s) = 1, \quad \lim_{\xi \rightarrow \infty} \hat{C}_1(\xi, s) = 0. \quad (\text{A.15})$$

757 Here we have denoted

$$\tilde{\kappa} = \frac{1}{2\mu_s}, \quad \tilde{\lambda} = \frac{\pi - \phi_0}{\phi_0} \cdot 2\mu_s. \quad (\text{A.16})$$

758 Now $\hat{C}_1$ can be solved from the Eqs. (A.14) and (A.15):

$$\hat{C}_1(\xi, s) = e^{\frac{1 - \sqrt{1 + 4\mu^2 F(s)}}{2\mu^2} \xi} \quad (\text{A.17})$$

759 where

$$F(s) = s(1 + \lambda \hat{\Lambda}(s)) + \tilde{\lambda} \sqrt{s(1 + \lambda \hat{\Lambda}(s))} \tanh \left(\tilde{\kappa} \sqrt{s(1 + \lambda \hat{\Lambda}(s))} \right). \quad (\text{A.18})$$

760 In order to find solution for the breakthrough curve $C_f(L, t)$, an inverse
 761 Laplace transform of $\hat{C}_1(1, s)$ has to be constructed. This can be done using
 762 the methods described by Kekäläinen [61]. The Laplace transform $\hat{C}_1(1, s)$
 763 is analytical outside the negative real axis and the inverse Laplace transform
 764 can be written as a Bromwich integral

$$C_1(1, \tau) = \lim_{R \rightarrow \infty} \frac{1}{2\pi i} \int_{-R}^R e^{\frac{1 - \sqrt{1 + 4\mu^2 F(iy)}}{2\mu^2}} e^{i\tau y} i dy. \quad (\text{A.19})$$

765 Using Cauchy's theorem the contour of integration can be changed as shown
 766 in Fig. A.7, and expression for $C_1(1, \tau)$ is obtained

$$C_1(1, \tau) = \lim_{R \rightarrow \infty} \frac{1}{2\pi i} \int_{\Gamma_R} e^{\frac{1 - \sqrt{1 + 4\mu^2 F(z)}}{2\mu^2}} e^{\tau z} dz. \quad (\text{A.20})$$

767 The integral in Eq. (A.20) can be expressed in a form

$$C_1(1, \tau) = \frac{\sqrt{2}}{\pi} \int_0^\infty e^{-G(x) - \tau x} \sin\left(\frac{\pi}{4} + H(x) - \tau x\right) dx, \quad (\text{A.21})$$

768 where

$$\begin{aligned} G(x) &= \frac{\text{Re} \sqrt{1 + 4\mu^2 F(-x + ix)} - 1}{2\mu^2} \\ H(x) &= \frac{\text{Im} \sqrt{1 + 4\mu^2 F(-x + ix)}}{2\mu^2}. \end{aligned} \quad (\text{A.22})$$

769 Using the formulas

$$\begin{aligned} \text{Re} \hat{\Lambda}(-x + ix) &= \frac{2}{\kappa} \sum_{n=1}^\infty \frac{2x^2 - x\alpha_n^2/\kappa^2}{(\alpha_n^2/\kappa^2 - x)^2 + x^2} \\ \text{Im} \hat{\Lambda}(-x + ix) &= \frac{2}{\kappa} \sum_{n=1}^\infty \frac{x\alpha_n^2/\kappa^2}{(\alpha_n^2/\kappa^2 - x)^2 + x^2}, \end{aligned} \quad (\text{A.23})$$

Figure A.7: Change of the contour of integration

and

$$\sqrt{x + iy} = \frac{\sqrt{x + \sqrt{x^2 + y^2}}}{\sqrt{2}} + i \frac{y}{\sqrt{2} \sqrt{x + \sqrt{x^2 + y^2}}}, \quad (\text{A.24})$$

$$\tanh(x + iy) = \frac{\sinh x \cosh x + i \sin y \cos y}{\cosh^2 x - \sin^2 y}$$

explicit expressions for $G(x)$ and $H(x)$ can be written. The expressions are relatively complicated but they can be easily implemented numerically. Numerical integration can be easily executed for $\tau \geq 1$ but for $\tau < 1$ (and small μ) the integrand is 'wildly oscillating' and the numerical integration fails. This is not a problem for physical applications since the breakthrough curve $C_1(1, \tau)$ for $\tau \gtrsim 1$ is of interest.

Appendix A.2. In situ -experiment

The model of the in-situ WPDE can be solved by modifying slightly the solution of the laboratory WPDE. A substitution of Eq. (A.2) with

$$C_0 = \frac{A_0}{\phi_0(2ab - b^2)L}, \quad (\text{A.25})$$

780 gives us dimensionless setup of the problem. The Eqs. (A.3) are the same but
 781 the radial diffusion equation for C_M is in the domain $1 < \rho < \rho_0$ ($\rho_0 = R/a$)
 782 and the dimensionless parameters are

$$\begin{aligned}\lambda &= \frac{2(\epsilon_p + (1 - \epsilon_p)\rho_r K_d)a}{2ab - b^2} \sqrt{\frac{D_a L}{v}}, \quad \kappa = a \sqrt{\frac{v}{D_a L}}, \\ \mu &= \sqrt{\frac{D_{eff}}{Lv}}, \quad \mu_s = \frac{1}{\pi - \phi_0} \sqrt{\frac{D \log(\frac{a}{a-b}) L}{2v(2ab - b^2)}}.\end{aligned}\tag{A.26}$$

783 In addition to the initial and boundary conditions Eq. (A.4), zero flux at
 784 boundary $\rho = \rho_0$ is applied:

$$\frac{\partial C_M^{(1)}}{\partial \rho}(\xi, \rho_0, \tau) = 0, \quad \frac{\partial C_M^{(2)}}{\partial \rho}(\xi, \psi, \rho_0, \tau) = 0.\tag{A.27}$$

785 Now the radial diffusion equations for $C_M^{(1)}$ and $C_M^{(2)}$ can be solved similarly
 786 by separating the variables:

$$\begin{aligned}C_M^{(1)}(\xi, \rho, \tau) &= C_1(\xi, \tau) + \pi \sum_{n=1}^{\infty} \frac{J_1(\alpha_n \rho_0)^2}{J_0(\alpha_n)^2 - J_1(\alpha_n \rho_0)^2} \\ &\quad \times (J_0(\alpha_n \rho) Y_0(\alpha_n) - Y_0(\alpha_n \rho) J_0(\alpha_n)) \int_0^{\tau} e^{-\frac{\alpha_n^2}{\kappa^2}(\tau-\sigma)} \frac{\partial C_1}{\partial \sigma}(\xi, \sigma) d\sigma, \\ C_M^{(2)}(\xi, \psi, \rho, \tau) &= C_2(\xi, \psi, \tau) + \pi \sum_{n=1}^{\infty} \frac{J_1(\alpha_n \rho_0)^2}{J_0(\alpha_n)^2 - J_1(\alpha_n \rho_0)^2} \\ &\quad \times (J_0(\alpha_n \rho) Y_0(\alpha_n) - Y_0(\alpha_n \rho) J_0(\alpha_n)) \int_0^{\tau} e^{-\frac{\alpha_n^2}{\kappa^2}(\tau-\sigma)} \frac{\partial C_2}{\partial \sigma}(\xi, \psi, \sigma) d\sigma,\end{aligned}\tag{A.28}$$

787 where the numbers $0 < \alpha_1 < \alpha_2 < \dots$ are the roots of the equation

$$J_1(\rho_0 \alpha) Y_0(\alpha) - Y_1(\rho_0 \alpha) J_0(\alpha) = 0.\tag{A.29}$$

788 From here on, the problem can be solved using exactly the same approach as
 789 in the previous case and the Laplace transform of C_1 has the same form as
 790 before in Eq. (A.14) but with different function Λ . In this case the Laplace
 791 transform of the function Λ is

$$\hat{\Lambda}(s) = \frac{2}{\kappa} \sum_{n=1}^{\infty} \frac{J_1(\alpha_n \rho_0)^2}{J_0(\alpha_n)^2 - J_1(\alpha_n \rho_0)^2} \cdot \frac{1}{s + \frac{\alpha_n^2}{\kappa^2}}.\tag{A.30}$$

792 Solving the Laplace transform of C_1 with boundary conditions Eq. (A.15)
793 leads to the solution same Eq. (A.17) as before, and the inverse Laplace
794 transform can be constructed in exactly the same way as in the case of the
795 laboratory experiment. When solving the breakthrough curves using Eq. 17,
796 the Eq. A.30 has to be used to get right expressions for $H(x)$ and $G(x)$ (see
797 Eq. A.22).