

***In situ* diffusion experiments: Effect of water sampling on tracer concentrations and parameters**

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Abstract. *In situ* diffusion experiments are performed at underground research laboratories (URL) in clay formations to overcome the limitations of laboratory diffusion experiments and investigate scale effects. Tracers are monitored in the circulation system by aliquoting the solution at selected times. The extracted samples may be replaced with the same volume of synthetic unspiked water as it is done in the Bure URL (France). Sampling with replacement induces the tracer dilution. In the sampling method used in the Mont Terri URL (Switzerland), on the other hand, sampling volumes are not replaced. In this case, there is no tracer dilution, but the volume in circulation decreases progressively. Water sampling is commonly disregarded in the numerical interpretation of such experiments. However, water sampling may induce changes in the tracer concentrations and errors in the estimated diffusion and sorption parameters. Such errors have been analyzed here with a numerical model which accounts for sample extraction, sample replacement and the changes in the volume of the circulation system. These errors have been analyzed for HTO, $^{36}\text{Cl}^-$, $^{22}\text{Na}^+$ and $^{134}\text{Cs}^+$ in the DIR2003 and EST 208 experiments at the Bure URL and for HTO, HDO, Br^- , $^{22}\text{Na}^+$, $^{85}\text{Sr}^{2+}$, $^{133}\text{Ba}^{2+}$ and $^{137}\text{Cs}^+$ in the DR experiments at the Mont Terri URL. The effect of water sampling on the relative tracer concentrations depends on the sampling method and frequency, the volume of the sample and the volume of the circulation system. Water sampling causes minor differences in relative tracer concentrations in the DR experiments and its effect can be disregarded. In the

DIR2003 experiment, however, the differences induced by aliquoting cannot not be neglected. $^{36}\text{Cl}^-$ is the tracer most affected by sampling and $^{134}\text{Cs}^+$ is the least influenced. The identifiability analysis of the EST208 experiment reveals that failing to account for the effect of water sampling may lead to a significant overestimation of diffusion and sorption parameters, especially for $^{36}\text{Cl}^-$. The results of our analysis indicate that the effects of the water sampling should not be neglected without a careful in-depth analysis.

Keywords: diffusion, sorption, numerical model, water sampling, DR experiments, DIR experiments, CORE

1. Introduction

Argillaceous rocks have been selected in many countries to host repositories for the disposal of radioactive waste. The diffusion and retention of radionuclides through such rocks are relevant for assessing the performance of repositories. Most of the experimental work in this field has focused on laboratory experiments performed on small samples. *In situ* diffusion experiments are performed at underground research laboratories (URL) in clay formations to overcome the limitations of laboratory diffusion experiments and to investigate possible scale effects. Such experiments have been performed in Opalinus clay in Switzerland (Palut et al., 2003; Tevissen et al., 2004; Wersin et al., 2004; van Loon et al., 2004; Yllera et al., 2004; Samper et al., 2006; Soler et al., 2008) and Callovo–Oxfordian clay at Bure in France (Dewonck, 2007; Dewonck et al., 2009).

In situ diffusion experiments in clay media involve several steps (Palut, 2001). First, tracers are diluted in a synthetic solution with a chemical composition similar to that of the formation porewater. Such water comes into contact with the clay formation in the injection chamber consisting of a borehole section isolated by packers. The injection chamber is located far enough from the gallery surface so that the test is performed on saturated clay not significantly disturbed by

the construction of the gallery. In order to avoid physical perturbations in the injection section, the hydraulic pressure is fixed to a value similar to the measured interstitial pressure of the formation. The tracers are let to diffuse in the rock. Tracer activities are monitored at the circulation system by aliquoting samples at selected times. After this step, the rock around the borehole where tracers have diffused is overcored. Rock samples are taken and analyzed. Tracer diffusion and sorption parameters are derived from tracer dilution and overcore concentration data.

Generally the effect of water sampling on the interpretation of *in situ* diffusion experiments is neglected when the total volume of the water samples is much smaller than the volume of the circulation system. Water samples extracted from the circulation system decrease the tracer mass, which may affect the evolution of relative tracer concentrations in a non negligible manner. Existing analytical and numerical methods for the interpretation of these experiments usually neglect water sampling. In some cases such as the DIR experiments at Bure URL the total volume of the samples is not negligible (CEA, 2008). Failing to account for the effect of the water sampling may induce errors in the estimated diffusion and sorption parameters. Such errors are analyzed here with a numerical model which accounts for sample extraction, sample replacement and the changes in the volume of the circulation system. The paper starts by describing the *in situ* diffusion experiments and the numerical methods used for their interpretation. The effect of water sampling on the DIR2003 experiment of Bure URL is described. Then, different sampling methods are compared for the conditions of the DIR2003 experiment. The relevance of the sampling volume and frequency is analyzed afterwards. Then, the effect of water sampling on the estimated parameters is discussed. Finally, the main conclusions are presented.

2. DIR and DR *in situ* diffusion experiments

The French National Agency for radioactive waste management (ANDRA) has undertaken an extensive characterization program at the Bure (Meuse/Haute-Marne) site in order to assess the feasibility of a deep high level waste repository in the Callovo-Oxfordian clay (Delay et al., 2007). Diffusion of inert and reactive tracers (DIR) is one of such experimental programs which aims at characterizing diffusion and retention of radionuclides in this formation.

Seven *in situ* diffusion experiments were performed in vertical boreholes in the Bure underground laboratory to derive diffusion and retention parameters of selected tracers. Experiments DIR2001, DIR2002 and DIR2003 have been carried out in boreholes drilled from a gallery located at a depth of ~450 m. Experiments DIR1001, DIR1002 and DIR1003 have been carried out in boreholes from a gallery located at ~490 m depth corresponding to the main level of the laboratory. Experiment EST208 is taking place in a 542.5 m depth borehole drilled from the ground surface.

DIR *in situ* diffusion experiments were performed as single-point dilution tests by injecting tracers into a 1 m long packed-off section into the boreholes. The required equipment included downhole and surface instrumentation (Palut, 2001). Downhole instrumentation consisted of a pneumatic packer system with a porous screen made of sintered stainless steel mounted just below the packer at the bottom of the borehole. Surface instrumentation included a stainless steel circuit to circulate the tracer solution and to allow for injection and sampling of tracers. The volume of synthetic water in the circulation system is about 10 L for all the DIR experiments. The tracer activities at the injection section were monitored during approximately 1 year for the following tracers: tritium (HTO), chloride (^{36}Cl), iodide (^{125}I), sodium ($^{22}\text{Na}^+$), strontium ($^{85}\text{Sr}^+$), selenium ($^{75}\text{Se}^{2+}$) and cesium ($^{134}\text{Cs}^+$). Chloride and iodide are subject to anion exclusion while sodium, strontium, selenium and cesium undergo sorption.

The design of the EST208 experiment differs from that of the DIR experiments because EST208 was performed in a deep borehole drilled from ground surface. Downhole instrumentation consists of a 10 m long packed diffusion interval with a stainless steel porous filter and two hydraulic lines for flux circulation. One allows the circulation from the diffusion chamber to the ground surface. The other ensures the water flow along the surface equipment used for monitoring the geochemical parameters and the extraction of water samples during the experiment. The circulation system contains 192.3 L of synthetic solution containing tritium (HTO), chloride ($^{36}\text{Cl}^-$) and cesium ($^{134}\text{Cs}^+$).

The injection section is composed of an empty central steel cylinder and a 3 mm thick steel filter between which the fluid containing the tracer cocktail circulates. There is a gap of 3 mm between the filter and the borehole wall. This gap is initially filled with artificial water injected during the hydraulic equilibration period. Later on, water in contact with argillite forms probably a viscous mud.

The DR experiment is an on-going *in situ* diffusion experiment within the Mont Terri Project (Mont Terri URL, Switzerland). This experiment is being performed in a borehole drilled into Opalinus clay normal to the bedding and focuses on the study of tracer retention and diffusion anisotropy. The two 15 cm long injection intervals are isolated by packers installed in the borehole. Each interval is connected to the surface equipment. The fluid circulates continuously, such that the tank water and the downhole water are always well mixed. The circulation system contains 20 L of synthetic porewater. The following tracers are injected in the upper interval: $^{60}\text{Co}^{2+}$, $^{137}\text{Cs}^+$, $^{133}\text{Ba}^{2+}$, $^{152}\text{Eu}^{3+}$, HDO. In the lower interval the tracers are HTO, $^{22}\text{Na}^+$, $^{85}\text{Sr}^{2+}$, I $^-$, Br $^-$, $^{75}\text{Se}^{4+}$ and ^{18}O . The injection of the tracer cocktails started in April 2006. Overcoring of the experiment took place at the beginning of 2010 (Fierz, 2006; Gimmi et al., 2009).

3. Numerical methods

The numerical interpretation of DIR experiments requires the use of 3D models due to diffusion anisotropy. However, symmetry with respect to the borehole axis allows the use of 2D axis-symmetric models. The relevance of diffusion anisotropy on tracer evolution at the test interval was evaluated by Samper et al. (2008a; 2008b) who concluded that these experiments can be safely interpreted with a 1D axisymmetric model. The gap and the filter are taken into account in the model. Therefore, five material zones are considered: the injection zone, the filter, the gap, a 2 cm thick excavation disturbed zone (EdZ) and the undisturbed Callovo-Oxfordian (COx) clay. The values of the effective diffusion, the accessible porosity and the distribution coefficient of each tracer in COx clay were derived from available through-diffusion laboratory experiments (Dewonck, 2007; Descostes et al., 2007). They are listed in Table 1. The distribution coefficient, K_d , for $^{22}\text{Na}^+$ in COx clay is assumed to be equal to 0.74 ml/g (Radwan et al., 2005). For $^{134}\text{Cs}^+$ a K_d of 50 ml/g was used. The effective diffusion coefficients for other materials were derived from those of undisturbed clay by adopting an Archie's law with an exponent equal to 4/3. The filter porosity is 0.3 (Dewonck, 2007). On the other hand, the porosities of the EdZ and the gap are unknown. As an educated guess, the porosity of the EdZ was assumed to be twice that of the clay while the porosity of the gap was assumed to be 0.6. The undisturbed clay and the EdZ were assumed to have the same distribution coefficient.

The diffusion anisotropy of the Opalinus clay is larger than that of the COx clay. Therefore, a 2D axis-symmetric model is needed to simulate and interpret the concentration of the tracers in the injection section (Samper et al., 2009; 2010). Several non-ideal factors must be taken into account such as the existence of the filter (3 mm thick), the gap (2 mm thick) between the filter and the borehole wall and the excavation disturbed zone (EdZ). Therefore, five material zones are

considered: the injection system, the filter, the gap, the EdZ and the undisturbed clay. The simulation of the DR experiment is performed for the reference values of the diffusion and sorption parameters of the tracer in the Opalinus clay. These values have been derived from laboratory experiments and previous *in situ* diffusion experiments and are similar to those of the COx clay. However, an anisotropy ratio of 4 has been considered.

4. Effect of sampling on computed concentrations at DIR2003 experiment

Tracers are monitored in the circulation system by aliquoting samples at selected times during the *in situ* diffusion experiment. Extracted samples are replaced with samples of the same volume of synthetic unspiked solution in experiments performed at Bure URL. In this way, the pressure and the volume of water in the circulation system remain unchanged during the experiment. However, a tracer dilution is induced by this replacement.

The tracer mass in the system after sampling, m_f , is equal to the initial mass before the water sampling, m_i , minus the mass contained in the water sample, m_s . Values of m_i and m_s can be expressed in terms of the concentration in the system before sampling, C_i , the total volume of the system, V , and the volume of the sample, V_s , through:

$$m_f = m_i - m_s = C_i (V - V_s) \quad (1)$$

The tracer concentration in the injection interval after water sampling, C_f , can be calculated from m_f and V through:

$$C_f = C_i \left(1 - \frac{V_s}{V}\right) \quad (2)$$

The dilution caused by sampling, ΔC , is given by:

$$\Delta C = C_f - C_i = -C_i \frac{V_s}{V} \quad (3)$$

The dilution depends on the volume of the circulation system, the tracer concentration before sampling and the volume of the aliquot. The effect of water sampling on tracer concentrations, C , is evaluated here in terms of the relative concentrations, $\frac{C}{C_0}$, where C_0 is the initial tracer concentration.

Therefore, aliquoting induces an instantaneous decrease of the tracer concentration in the circulation system (Figure 1). At that time, the tracer concentration in the injection section is smaller than the concentration in the rock at the vicinity of the borehole. Thus, a mass flux from the rock to the borehole takes place during a short period of time until both concentrations reach a similar value. In addition, the decrease of the tracer concentration in the injection interval decreases the concentration gradient between the borehole and the rock and slows down the tracer diffusion from the borehole into the rock. Although the effect of taking several samples is cumulative, the total difference in computed concentrations at the circulation system is not simply equal to the sum of the differences caused by each aliquot. Quantifying the effect of water sampling requires the use of a numerical model accounting for sample aliquoting and replacement.

The relevance of water sampling on relative tracer concentrations for the DIR2003 experiment has been evaluated here by analyzing the differences in relative concentrations computed with simulations which either ignore or take into account the water sampling. Simulations are performed with the same 1D axi-symmetric model used for the interpretation of dilution data (Samper et al., 2008a). The simulation is interrupted at each sampling time and relative tracer concentrations are adjusted according to the dilution ΔC of Eq. 3. Aliquots have volumes of either 25 or 75 ml.

HTO was injected at the beginning of the DIR2003 experiment. $^{36}\text{Cl}^-$, $^{22}\text{Na}^+$ and $^{134}\text{Cs}^+$ were injected 434 days later. This feature of the DIR2003 experiment allow us to study the effect on the dilution of HTO of the second injection of tracers and the intensive sampling associated to such injection. Figure 2 shows the comparison of the dilution curves for the entire experiment and all the tracers computed with and without sampling for each tracer. There is a clear discontinuity in the dilution curve of HTO caused by the large number of samples taken just after the second tracer injection.

The differences in the relative tracer concentrations computed with and without water sampling for the DIR2003 experiment are listed in Table 2. For conservative tracers the differences in computed concentrations increase with time. After 1 year, tracers are not affected in the same way. $^{36}\text{Cl}^-$ is the tracer most affected with a difference in relative concentrations of 0.074. For HTO, $^{22}\text{Na}^+$ and $^{134}\text{Cs}^+$ the differences are equal to 0.033, 0.013 and 0.0002, respectively. The stronger the sorption, the smaller the effect of water sampling. Eq. 3 provides the hints to explain the different effects of sampling on the concentrations of each tracer. Though the volume of the system and the sampling volumes are the same for all the tracers, the concentration in the circulation system before sampling, C_i , is different for each tracer depending on its diffusion and sorption properties. The slower the dilution of a tracer, the larger its concentration before sampling, C_i , and therefore, the larger the effect caused by the water sampling.

5. Comparison of sampling methodologies at DIR2003 experiment

The sampling methodologies used in the *in situ* diffusion experiments in Mont Terri and Bure URL's are different. In Mont Terri water samples are not replaced. The reduction in water pressure caused by the decrease of water in the circulation system is equilibrated by injecting gases. In this

case there is no direct tracer dilution, but a progressive reduction of the volume of the circulation system, V , which speeds up the tracer dilution.

Sampling methods with and without replacement have been compared for the conditions of the DIR2003 experiment. The experiment has been simulated by taking into account actual sampling volumes and dates. Figure 3 shows the computed dilution curves of $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ for: 1) No sampling, 2) Sampling with replacement and 3) Sampling with no replacement. Table 3 shows the differences in relative tracer concentrations computed with and without sampling at $t = 1$ year for each type of water sampling procedure (with and without volume replacement). Tracers suffering from anion exclusion are the most affected by the water sampling in both types of methods. On the other hand, water sampling has the smallest effect on the curves of the sorbing tracers. Other things being the same, the replacement of the water samples leads to differences which are larger than those of the no-replacement case for $^{36}\text{Cl}^-$ and HTO. For $^{22}\text{Na}^+$, however, the difference is larger in the case where the samples are not replaced.

In addition to sampling, γ -emitter tracers can be monitored online with γ -counting techniques which were successfully tested in the DI-A and DR experiments at the Mont Terri URL (Fierz, 2006; Gimmi et al., 2009). On-line measurement of tracer activities in the circulation system provides a way to reduce the sampling frequency and the effect of the water sampling on tracer dilution data.

6. Relevance of the sampling volume and frequency

Aliquoting affects the relative tracer concentrations in the DIR2003 experiment in a significant manner. The effect of water sampling on tracer concentrations depend on: 1) The diffusion and sorption properties of each tracer, 2) The sampling method (with or without replacement), 3) The

sampling frequency, 4) The volume of the samples and 5) The volume of the circulation system. The first two factors were analyzed in previous sections. Here the influence of the other three is analyzed by analyzing the effect of water sampling in diffusion experiments having different designs such as the DIR2003, the EST208 and the DR experiments.

The EST208 experiment is being performed in a 10 m long packed diffusion interval of a deep borehole. The volume of the circulation system is about 20 times larger than that of the DIR2003 experiment. The sampling frequency is similar for both experiments but the EST208 sample volume is 150 ml which is twice as much as that of DIR2003 experiment. HTO, $^{36}\text{Cl}^-$ and $^{134}\text{Cs}^+$ are used as tracers. The differences in relative tracer concentrations in the injection interval computed with and without sampling for the EST208 experiment are listed in Table 4. These differences in concentrations are much smaller than those obtained for the DIR2003 experiment. It should be noticed that the ratio V_s/V for the EST208 experiment is much smaller than that of the DIR2003 experiment. Therefore, the dilution caused by water sampling is less relevant for the EST208 experiment than in the DIR2003 experiment. At $t = 3$ years the differences are smaller than 0.02 for all the tracers. On the other hand, $^{36}\text{Cl}^-$ is the tracer most affected while $^{134}\text{Cs}^+$ is the least influenced.

The effect of water sampling has also been analyzed in the DR experiments where extracted sample volumes are small and are not replaced. The effect of sampling has been neglected in all the previous modelling tasks performed for this experiment because the total volume of the samples is smaller than the volume of the circulation system, $V \sim 20$ L. The effect of water sampling in the relative concentrations has been evaluated for the DR experiments using a numerical model which takes into account the changes in the volume of the circulation system. Dates and sample volumes have been considered for the first 1106 days. The differences in relative concentrations in the injection interval at $t = 3.6$ years computed with and without sampling are listed in Table 5. The

differences in relative tracer concentrations caused by sampling are equal or smaller than 0.01 for all the tracers. Such errors are smaller than those computed for the DIR2003 experiment at $t = 1$ year by assuming no water replacement (Table 3). These results are consistent with the values of $\frac{V_s}{V}$ of these experiments. Sample volumes in the DR experiments are smaller than those of the DIR2003 experiment while the volume of the circulation system of the DR experiments is twice of that of the DIR2003 experiment.

7. Effect of sampling on estimated parameters

Synthetic experiments have been used to study parameter identifiability and parameter uncertainties at DIR2001, DIR2002 and EST208 (Samper et al., 2008a). Synthetic data have been generated in order to provide insight on the inverse estimation of diffusion and sorption experiments and to study parameter identifiability. Key diffusion parameters have been estimated from noisy synthetic data generated with a numerical model having known parameters. Here we present the identifiability analysis to evaluate the parameter estimation errors caused by failing to account for the water sampling. A synthetic diffusion experiment having the same geometric properties as the real EST208 experiment was simulated. This model takes into account the water sampling.

Parameters are estimated from synthetic data using a numerical model which neglects sampling. Inverse runs are performed with INVERSE-CORE^{2D} (Dai and Samper, 2004) following a systematic approach according to which: 1) The D_e of the filter and the D_e of the gap are estimated first using early-time data collected during the first 10 days; 2) Then, the D_e of the filter and the D_e of the gap are fixed to their estimated values and the D_e of the EdZ and the accessible porosity of the EdZ are estimated using concentration data measured until 50 to 100 days; 3) The D_e and the accessible porosity of the undisturbed clay are estimated using all the concentration data while the

remaining parameters are fixed to values estimated in steps 1 and 2. Since true values are known and data are free of noise, one can compute the parameter estimation error caused by failing to account for the water sampling. The D_e of the undisturbed clay for HTO is overestimated by 10%. A good fit to $^{36}\text{Cl}^-$ data is obtained with values of the D_e of the undisturbed clay and the EdZ which are overestimated by 10 to 20% and unrealistically too large accessible porosities of the EdZ and the rock (Figure 4). These large estimation errors for $^{36}\text{Cl}^-$ dilution data are caused by the large effect of water sampling on $^{36}\text{Cl}^-$ dilution data and by the poor identifiability of the parameters of this tracer when data contain noise (Samper et al., 2008a). If accessible porosities are fixed to their true values, the estimation errors of the D_e of the clay and the EdZ are even larger than before.

Errors in computed concentrations with and without sampling after 1 year for $^{134}\text{Cs}^+$ are smaller than 1%. Therefore, estimation errors of diffusion and sorption parameters are small.

8. Conclusions

The effect of water sampling in relative tracer concentrations in the injection interval of *in situ* diffusion experiments has been analyzed with a numerical model which accounts for sample extraction, sample replacement and the changes in the volume of the circulation system. These effects have been analyzed for HTO, $^{36}\text{Cl}^-$, $^{22}\text{Na}^+$ and $^{134}\text{Cs}^+$ in the DIR2003 and EST 208 experiments at the Bure URL and for HTO, HDO, Br^- , $^{22}\text{Na}^+$, $^{85}\text{Sr}^{2+}$, $^{133}\text{Ba}^{2+}$ and $^{137}\text{Cs}^+$ in the DR experiments at the Mont Terri URL. The effect of the water sampling on tracer concentrations depend on: 1) The sampling method (with or without replacement of the volume of the sample); 2) The sampling frequency; 3) The volume of the sample; and 4) The total volume of the circulation system.

It has been found that water sampling in the DR experiments causes minor changes in the relative tracer concentrations. Therefore, its effect can be disregarded. In the DIR2003 experiment,

however, the differences induced by the water sampling cannot be neglected. After 1 year, $^{36}\text{Cl}^-$ is the tracer most affected by sampling with a difference in relative concentration equal to 0.074. $^{134}\text{Cs}^+$ is the least affected with a very small difference. Furthermore, the simulation of this experiment shows that a second injection of tracers and the intensive sampling associated with it generates a clear discontinuity in the dilution trend of the tracer. The identifiability analysis of the EST208 experiment reveals that failing to account for the effect of water sampling may lead to a significant overestimation of diffusion and sorption parameters, especially for $^{36}\text{Cl}^-$.

The results of our analysis indicate that the effects of the water sampling should not be neglected without a careful in-depth analysis. They also provide practical guidelines for optimizing the tracer sampling of *in situ* diffusion experiments. Therefore, the effect of sampling can be minimized regardless the sampling method by optimizing the design of the experiment. If the design of the experiment is not optimized, the sampling effect can be reduced by using on-line tracer monitoring techniques.

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