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Case Study

# Modelling radionuclide transport in fractured media with a dynamic update of $K_d$ values

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ABSTRACT

Radionuclide transport in fractured crystalline rocks is a process of interest in evaluating long term safety of potential disposal systems for radioactive wastes. Given their numerical efficiency and the absence of numerical dispersion, Lagrangian methods (e.g. particle tracking algorithms) are appealing approaches that are often used in safety assessment (SA) analyses. In these approaches, many complex geochemical retention processes are typically lumped into a single parameter: the distribution coefficient ($K_d$). Usually, the distribution coefficient is assumed to be constant over the time frame of interest. However, this assumption could be critical under long-term geochemical changes as it is demonstrated that the distribution coefficient depends on the background chemical conditions (e.g. pH, Eh, and major chemistry). In this work, we provide a computational framework that combines the efficiency of Lagrangian methods with a sound and explicit description of the geochemical changes of the site and their influence on the radionuclide retention properties.



## 1. Introduction

Crystalline rock formations are under consideration by several countries as host formations for geological disposal of radioactive wastes. Over the long time frames of interest in assessing safety of those potential disposal systems, environmental conditions are expected to change. Such changes are expected to be particularly dramatic for repositories located at high latitudes. For example, the prospective Finnish and Swedish repositories (Posiva, 2013; SKB, 2013) for spent nuclear fuel are expected to see climatic changes from temperate to periglacial and eventually to glacial conditions over a 100,000 year period. Such changes will significantly alter the hydrological and geochemical conditions in the host rock.

A key component of the aforementioned safety assessment (SA) studies is the analysis of possible releases of radionuclides from a canister in a deposition hole and their transport along preferential flow paths in the fractured rock. This analysis is typically carried out by means of radionuclide transport simulations. In the last Swedish and Finnish safety analyses (i.e. SR-Site, SKB, 2011, and TURVA2012, Posiva, 2012), most of these calculations were carried out using the time domain particle tracking code Migration Analysis of Radionuclides in the Far Field (MARFA) (Painter et al., 2008; Painter and Mancillas, 2013). MARFA uses a numerically efficient algorithm, which allows complex calculations to be carried out relatively quickly. This efficiency is particularly appealing in SA studies, where typically a large number of variant simulations are required. Besides computational efficiency, MARFA is free of numerical dispersion, which means that computed breakthrough curves are not affected by spurious effects such as artificial dilution. A summary of MARFA's processes and conceptualizations and of the variant versions developed for this work is presented in Appendix A.

As in most of the Lagrangian-based transport codes (e.g. Salamon et al., 2006, and references there in), in MARFA sorption reactions are represented using distribution coefficients ($K_d$), which are usually kept unchanged over the simulation time frame. It is worthwhile noting that $K_d$-based transport calculations are not suited to describe chemical retention processes other than sorption (e.g. the precipitation of radionuclides in minerals or solid solutions).

The dependence of specific contaminant distribution coefficients on the underlying background geochemical conditions (i.e. pH, redox conditions, salinity, and TDS) has been widely studied

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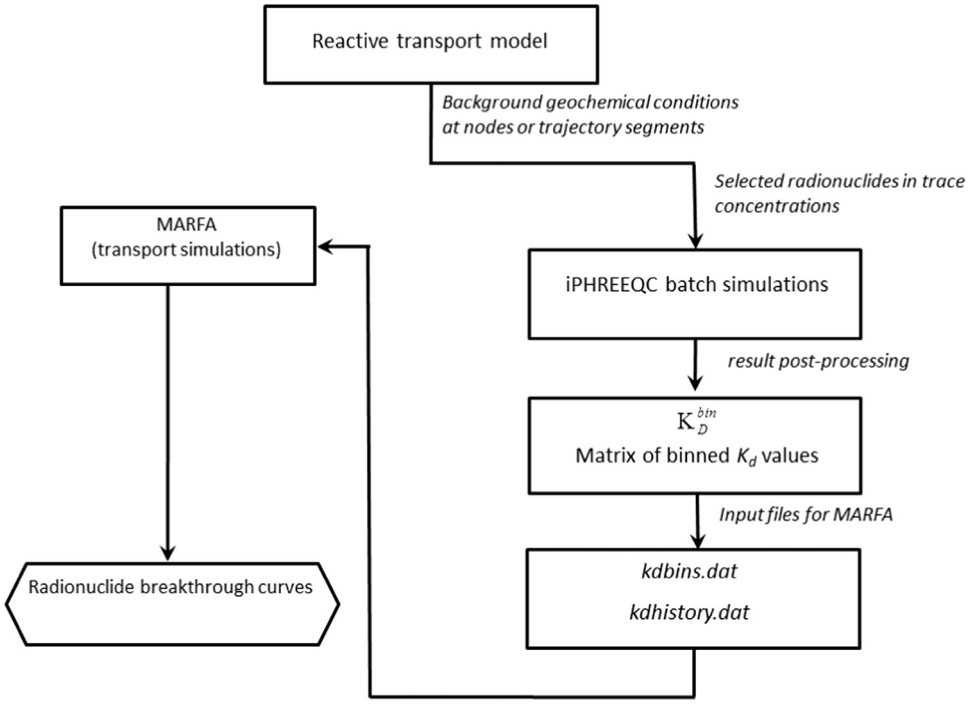


**Fig. 1.** Functionality overview of iFM.

and documented (e.g. Abril, 1996; Sauve et al., 2000; Crawford et al., 2006; Granizo and Missana, 2006; Domènech et al., 2015). Different numerical studies have made attempts to keep track of this dependency in $K_d$-based radionuclide transport simulations using the so-called "smart $K_d$" approach (e.g. Stockmann et al., 2012; Flügge et al., 2013; Noseck et al., 2014). In these works the computationally expensive reactive transport calculations that are needed to determine spatial and temporal variations in $K_d$'s are performed using simplified geochemical calculations, where environmental markers (e.g. $H^+$ and ionic strength) are transported and affected by simplified reactions. These calculations are coupled to the $K_d$-based radionuclide transport simulations.

Here we propose an alternative and novel formulation of the "smart $K_d$" approach, which relies on two basic premises: (i) the evolution of the background geochemistry need to be described in its full complexity as "individual sub-processes cannot be fully assessed without considering them in the context of the other dynamic processes" (Steefel et al., 2005) and (ii) radionuclide transport calculations need to be efficient and free of numerical dispersion.

In the proposed methodology, the mutual interplay between physical and (bio)geochemical processes and their effect on the hydrochemical conditions of the site under study are captured by means of mechanistic multicomponent reactive transport calculations. This, which is an important difference of the methodology compared to the previously cited "smart $K_d$" approaches, allows the full complexity and non-linearity of the system to be consistently included in the numerical framework.

The requirements of numerical efficiency and absence of numerical dispersion are achieved by decoupling the simulation of radionuclide transport from the calculation of the background geochemistry, under the hypothesis that radionuclides are in trace concentration. This allows radionuclide transport calculations to be efficiently carried out using MARFA and this, in turn, allows specific uncertainties (e.g. release location and retention model) to be treated in a probabilistic fashion. Other types of uncertainties, related to the evolution of the background geochemistry, are more difficult to represent as the underlying model is built upon computationally expensive mechanistic reactive transport calculations.

## 2. Methodological approach

The basic premise of the approach is that the radionuclides are in trace concentration, which implies that (i) they do not affect the evolution of the background geochemistry and (ii) their retention is linear with concentration. Given this assumption, the methodology follows these steps:

1. The evolution of the background geochemistry is computed using a mechanistic flow and reactive transport code.
2. The computed chemical solutions (i.e. concentration of aqueous species, including redox conditions and temperature, at each node of the domain and at each considered time step), the selected sorption model and an arbitrarily low radionuclide concentration are used to carry out mechanistic 0D batch calculations.
3. The results provide a database of distribution coefficients (in space and time) that is used to dynamically update the $K_d$ values used in the MARFA radionuclide transport simulation.

The retention model (Step 2) is defined by the user and has to be representative of the actual mineralogy of the site under study.

Steps 2 and 3 are run automatically using a numerical tool, denoted as iFM (interface to MARFA). iFM is a python script that takes care of the following operations:

A: The chemical solutions are retrieved from the results of step 1 and stored in memory.
B: The sorption model is read from the user configuration file.
C: For each chemical solution, a batch calculation is performed using the dynamic library IPhreeqc (Charlton and Parkhurst, 2011). In the calculation, an arbitrarily low radionuclide concentration is added to the solution and the resulting aqueous composition is equilibrated with the sorption sites.

D: The resulting radionuclide distribution coefficient is stored in memory.
E: To keep the MARFA input files at an acceptable level of size and complexity, the full $k_d$ matrix (i.e. one value of $K_d$ for each location and calculation time) is binned (i.e. the computed $K_d$ values are categorized into equal-sized bins; with the number of bins being a parameter that is user defined) and post-processed in the form of an ASCII file that is input to MARFA.

A workflow of iFM is shown in Fig. 1. A new version of MARFA was created in order to accommodate time-varying $K_d$ values. Details of this new version are presented in Appendix A.

## 3. Verification examples

The verification tests simulate the release and transport of strontium from a potential deep geological repository. The reactive transport problem is solved using the methodology described in Section 2. Independent solutions, based on fully coupled reactive transport models, are used for the verification.

### 3.1. Models set-up

Most of the radionuclide transport calculations used in SA studies are carried out along fixed networks of streamlines, and mass exchange and mixing processes between adjacent streamlines are usually neglected (e.g. SKB, 2011; Posiva, 2012). This approach is conservative as natural attenuation processes due to dilution are not accounted for.

Groundwater flow simulations of periods of glaciation/de-glaciation events are reproduced assuming different positions of the ice front (e.g. Vidstrand et al., 2010; Löfman and Karvonen, 2012). Simplifying the problem, one can say that when the ice margin reaches the repository area, diluted glacial water starts to infiltrate and in some cases (e.g. when the ice front stays for a longed period on top of the repository), the signature of the glacial water may reach repository depth. Then, when the ice front retreats, altered meteoric water starts to infiltrate in the shallow bedrock and flushes away the glacially derived groundwater.

Here, we verify the proposed methodology by solving a simplified radionuclide transport problem under variable geochemical conditions caused by changes in the climatic conditions. The radionuclide transport calculations are carried out along single (Section 3.2) or multiple (Section 3.3) streamlines. Radionuclides are introduced into the system during a small time interval compared to the time frame of the problem (i.e. the injection can be considered as a Dirac $\delta$-function). Initially, glacial conditions are assumed to prevail in the whole domain, which consists of single or multiple streamlines that connect the release boundary to the surface. At $t = 20, 100$ years a different and less diluted water, representative of new temperate conditions, enters the model domain from the release boundary and propagates along the streamline(s). The two waters used in the reactive transport simulations are listed in Table 1. These two waters were previously used by Salas et al. (2010) to assess numerically the hydro-chemical evolution at the Forsmark site (Sweden). Equilibrium with pyrite and calcite is considered.

A cation exchange model, borrowed from Bradbury and Baeyens (2000), is used to simulate the sorption of strontium. In this model, the most abundant sites ( ≈80% of cation exchange sites) are the so-called Planar Sites, which are considered to be of low affinity and can adsorb either divalent species or monovalent cations. The second and third types of sites, called Type II and Frayed Edge Sites (FES), respectively, the surface fractions of which are 20% and 0.25% of the total sites, involve monovalent cations

**Table 1**
Chemical composition of the two groundwaters used in the reactive transport calculations. The glacial groundwater is used as initial water. The temperate groundwaters enter the model domain at $t = 20, 100$ years. The waters are taken from Salas et al. (2010).

| | Glacial groundwater | Temperate groundwater |
|---|---|---|
| pH | 10.1 | 6.84 |
| pe | −6.6 | −2.6 |
| Total concentration (mol/L) | | |
| Ionic strength | $6.8 \times 10^{-4}$ | $1.3 \times 10^{-1}$ |
| Cl | $2.4 \times 10^{-5}$ | $1.0 \times 10^{-1}$ |
| Ca | $9.5 \times 10^{-5}$ | $1.8 \times 10^{-2}$ |
| Na | $1.1 \times 10^{-5}$ | $6.1 \times 10^{-2}$ |
| S | $3.8 \times 10^{-4}$ | $2.2 \times 10^{-3}$ |
| Mg | $9.9 \times 10^{-5}$ | $4.7 \times 10^{-3}$ |
| K | $9.2 \times 10^{-6}$ | $8.0 \times 10^{-4}$ |
| Fe | $1.9 \times 10^{-5}$ | $5.8 \times 10^{-5}$ |
| Si | $1.7 \times 10^{-7}$ | $4.7 \times 10^{-4}$ |
| C | $1.9 \times 10^{-4}$ | $4.8 \times 10^{-3}$ |

**Table 2**
Cation exchange reactions and Gaines–Thomas selectivity coefficients.

| Reaction | log K (25 °C) | Reference |
|---|---|---|
| *Planar sites* | | |
| $X^- + Na^+ \leftrightarrow NaX$ | 0.0 | Bradbury and Baeyens (2000) |
| $X^- + K^+ \leftrightarrow KX$ | 1.1 | Bradbury and Baeyens (2000) |
| $2X^- + Sr^{2+} \leftrightarrow SrX_2$ | 1.13 | Brouwer et al. (1983) |
| $2X^- + Ca^{2+} \leftrightarrow CaX_2$ | 1.13 | Brouwer et al. (1983) |
| $2X^- + Mg^{2+} \leftrightarrow MgX_2$ | 1.13 | Brouwer et al. (1983) |
| *Type* II *sites* | | |
| $X^{II-} + Na^+ \leftrightarrow NaX^{II}$ | 0.0 | Bradbury and Baeyens (2000) |
| $X^{II-} + K^+ \leftrightarrow KX^{II}$ | 2.1 | Bradbury and Baeyens (2000) |
| *FES* | | |
| $X^{FES-} + Na^+ \leftrightarrow NaX^{FES}$ | 0.0 | Bradbury and Baeyens (2000) |
| $X^{FES-} + K^+ \leftrightarrow KX^{FES}$ | 2.4 | Bradbury and Baeyens (2000) |

only. The cation exchange reactions and related Gaines–Thomas selectivity coefficients used in the model are listed in Table 2 and the considered number of cation exchange sites, CES, is $4.5 \times 10^{-3}$ mol/L. It is worthwhile noting that this value, which in real applications is highly uncertain, has an important effect on the competitive sorption of radionuclides.

All the batch calculations have been carried out using PHREEQC with the SKB thermodynamic database (SKB-TDB). This database was developed by Hummel et al. (2002) with modifications by Duro et al. (2006).

### 3.2. Single trajectory

A single streamline with travel time, $\tau$, equal to 2664 years divided into 210 equal-time segments, was used for the first verification test. The evolution of the background geochemistry along the streamline was computed using PHREEQC (Parkhurst and Appelo, 2013). Results were retrieved by iFM and processed according to the methodology described in Section 2. Radionuclide transport was then simulated with MARFA using an equilibrium sorption model. In these MARFA calculations, distribution coefficients were dynamically updated with the information provided by iFM.

An independent solution was also computed by running the fully coupled problem (i.e. radionuclide transport and evolution of background geochemistry) with PHREEQC. Moreover, to evaluate

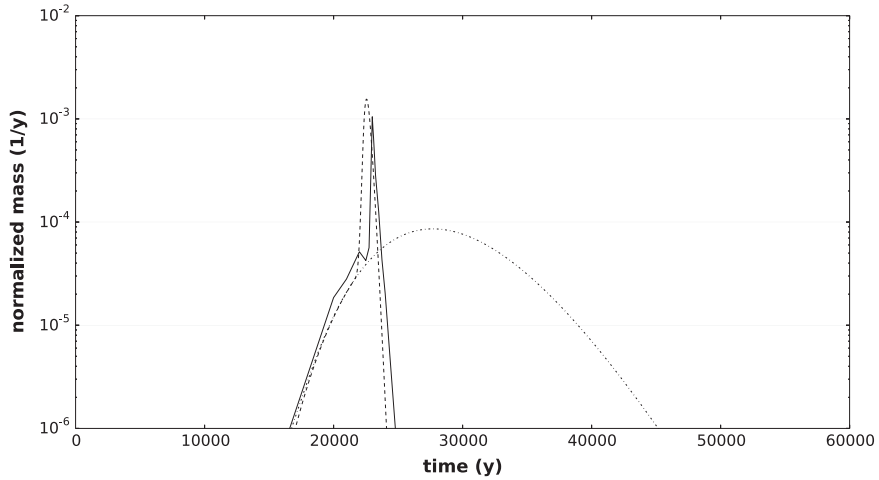


**Fig. 2.** Strontium breakthrough curve at the outlet of the streamline. The results of the MARFA simulation with dynamic update of $K_d$ values (solid line) are compared to the independent fully coupled reactive transport simulation (dashed line). The independent simulation has also been run considering unchanged background geochemical conditions during the whole time frame (dashed dotted-line).

the effect of the geochemical perturbation, an additional independent solution was computed, where the geochemical conditions remain unchanged during the whole time frame.

The results of the radionuclide transport calculations (Fig. 2) show that when strontium is overtaken by the geochemical perturbation, it is mobilized and moves nearly unretarded. This effect is attributable to the very different ionic strengths of the two selected groundwaters. The glacial groundwater type is very diluted (ionic strength equal to $6.8 \times 10^{-4}$ M) whereas the temperate groundwater type has a considerably higher ionic strength ($1.3 \times 10^{-1}$ M). It turns out that, when glacial conditions prevail, the radionuclides are strongly sorbed due to the relatively low competition for the available sorption sites. On the contrary, when temperate conditions are attained, much more cations compete for the same exchange sites and thus the retention of strontium decreases dramatically. This effect is captured by both MARFA and the independent simulation. The agreement between the two solutions is good and minor differences are likely caused by the fact that the independent solution is affected by some numerical dispersion and the binning of the $K_d$ values. In addition, MARFA's solution method is of the Monte Carlo type and thus includes some statistical uncertainty. Moreover, MARFA reconstructs breakthrough curves from the particle arrival times and this reconstruction can smooth sharp peaks slightly.

### 3.3. Multiple trajectories

Here, we solve a typical radionuclide waste safety assessment problem: the simulation of the migration of radionuclides (i.e. strontium) from a deep geological repository to the surface along a set of streamlines, which mimic a network of preferential flow paths in a fractured medium.

A snapshot of a groundwater velocity field was taken from an existing regional-scale three-dimensional hydrogeological model. Using the code RW3D (Fernandez-Garcia et al., 2005), 3960 particles were injected at repository depth and tracked to the surface of the model domain (Fig. 3). As the particles move with the flow field without interacting with the rock matrix, they represent the trajectories of potential transport pathways connecting the repository area to discharge points into the biosphere. The distribution of travel times for the 3960 streamlines is shown in Fig. 4.

The conceptual model is the same as explained in Section 3.1. Initially, glacial conditions prevail in the whole domain. At time

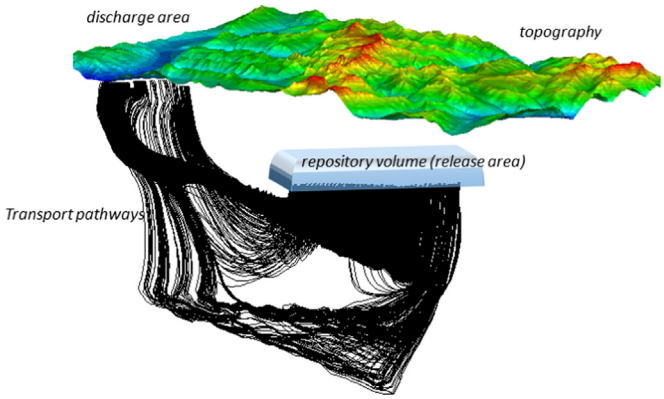


**Fig. 3.** Set of 3960 transport pathways used in the verification exercise.

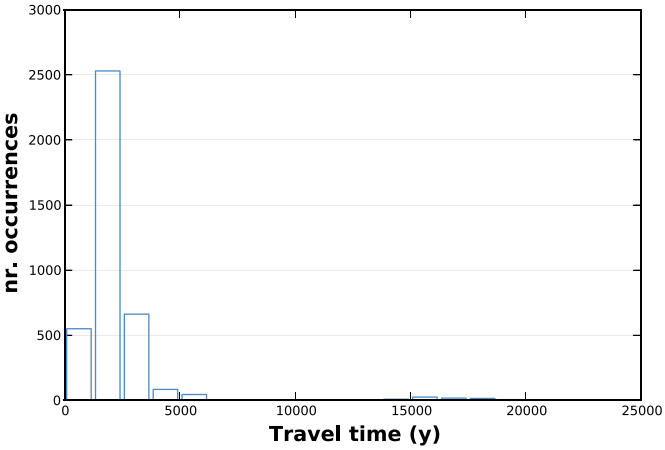


**Fig. 4.** Histogram of advective travel time for the 3960 streamlines representing transport pathways.

20,100 years, a change in the boundary conditions (from glacial to temperate water) occurs at repository depth and propagates along the streamlines. The radionuclides enter the model domain at time zero from repository depth. This radionuclide injection occurs during a time interval that is small compared to the transport times of the problem.

The evolution of the background geochemistry along the multiple trajectories was simulated using FASTREACT (Trinchero et al., 2014). FASTREACT is a stochastic-convective-based framework that

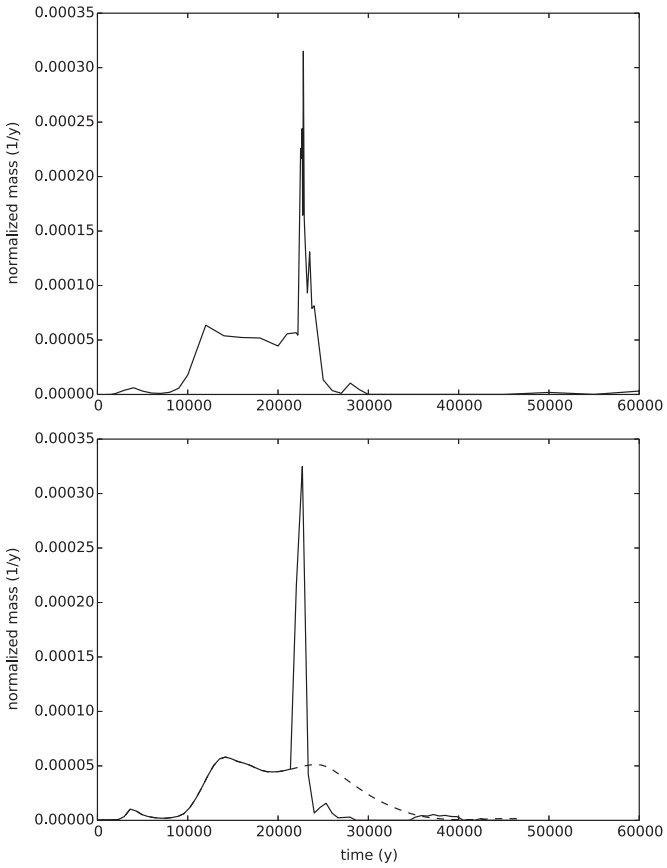


**Fig. 5.** Strontium breakthrough curve for the ensemble of flow paths computed using (top) MARFA with variable $K_d$ values and (bottom) FASTREACT. A FASTREACT simulation with constant geochemical background conditions (i.e. glacial conditions) is also included (dashed line).

makes use of a single PHREEQC reactive transport simulation to provide breakthrough curves for ensemble of particle trajectories and to compute the chemical evolution at any segment of any considered trajectory. The breakthrough curves are obtained as the convolution of the concentration computed using the single reference calculation and the travel time probability density distribution, which is inferred from the considered set of trajectories. The hydrochemical evolution of a considered trajectory segment is obtained by relating its travel time to that of the corresponding grid cell of the reference simulation. Further details of FASTREACT are provided in Trinchero et al. (2014). The results of FASTREACT were then retrieved and processed by iFM. Finally, a MARFA calculation was carried out using an equilibrium sorption model. In this calculation, $K_d$ values were updated using the information provided by iFM.

An independent solution was also computed by solving the full reactive transport problem (i.e. the evolution of background geochemistry and the radionuclide transport) using FASTREACT.

The results of the simulations (Fig. 5) are qualitatively similar to what is observed for the single streamline: strontium moves slowly until it is overtaken by the geochemical perturbation front. When background conditions change, from glacial to temperate, the retention of strontium decreases dramatically and a sharp peak is observed at $t \approx 22,700$ years. The effect of the geochemical perturbation, which results in mobilization of strontium, is captured by the two solutions and their overall match is good. Minor differences are likely due to numerical dispersion in FASTREACT, the binning and interpolation of the $K_d$ values, and by MARFA's algorithm for reconstructing breakthrough curves from particle histories, which may slightly reduce the peak breakthrough. In addition, MARFA uses a Monte Carlo type of algorithm and thus contains statistical noise.

## 4. A demonstration simulation

Recently, a high performance computing (HPC) reactive transport simulation has been carried out to study the formation and migration of a hyper-alkaline plume produced by the dissolution of the grout used during the construction of the future deep geological repository of Forsmark (Sweden). The groundwater flow problem was solved using the finite volume hydrogeological code DarcyTools (Svensson et al., 2004). An existing discrete fracture network (DFN) was first upscaled over the underlying grid, which was discretized with high accuracy using regular hexahedron elements of size 4 m $\times$ 4 m $\times$ 2 m, resulting in a highly heterogeneous conductivity field (Fig. 6). The computed groundwater velocity field, which was assumed to be at steady state, was then imported into PFLOTRAN (Lichtner et al,. 2013a,b) using the developed interface, denoted as iDP (interface DarcyTools-PFLOTRAN, Molinero et al., 2015). An important implication of this assumption is that changes in permeability and porosity caused by the dissolution of the grout and the precipitation of secondary minerals are neglected. Representative groundwater types of Forsmark were used to mimic the initial hydrochemical conditions in the shallow (from surface to 200 m depth – mix of the water types “Altered Meteoric” and “Littorina” groundwaters, with a Cl concentration of 0.03 M) and in the deep (from 200 m depth to bottom – mix of the water types "Altered Meteoric" and "Littorina" groundwaters, with a Cl concentration of 0.15 M) part of the domain. Those grid cells belonging to the repository access tunnels and having a permeability higher than a given threshold were assumed to be grouted (Fig. 7). Thus, in these cells, portlandite and the calcium silicate hydrate phase CSH-1.8 were considered, each of them with an initial volume fraction of $5{\cdot}10^{-4}$. The dissolution of grout leads to the formation of a high pH plume. The PFLOTRAN reactive transport simulation, whose grid was composed of 105,044,948 cells and whose simulation time frame was 20,000 years, was run on the supercomputer called “MareNostrum” and took place over 15 days using 2.77 million CPU hours. For further details on the actual set-up of the reactive transport simulation, which is here denoted as Grand Challenge – GC – model, the reader is referred to de Vries et al. (2013, 2014) and Molinero et al. (2015).

Here, we use the results of the GC model (i.e. evolution of background geochemistry) to perform synthetic simulations of radionuclide transport using iFM and MARFA. In order to make the radionuclide transport exercise illustrative for this numerical framework, we selected cesium and a model for radionuclide sorption (i.e. cesium sorption onto magnetite, Granizo and Missana, 2006) with a strong and evident pH dependency (in the GC model,

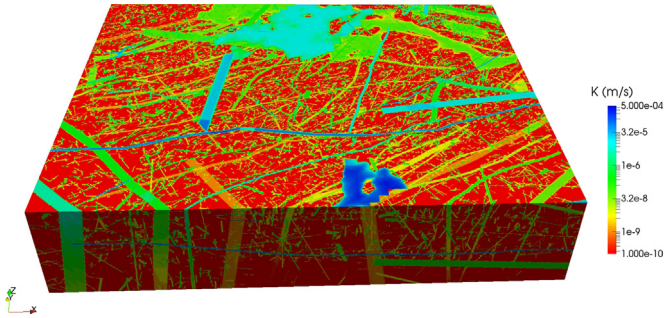


**Fig. 6.** Hydraulic conductivity field for the Forsmark spent fuel repository area generated by DarcyTools (figure taken from Molinero et al. (2015)).

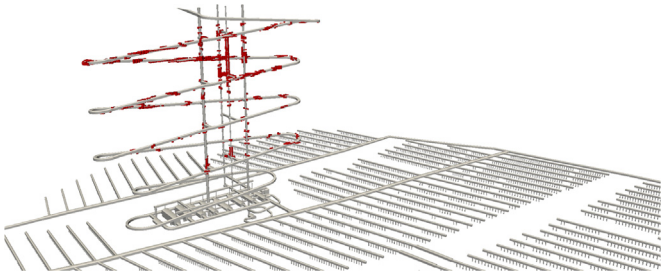

**Fig. 7.** Details of the initially grouted cells of the GC model (results taken from Molinero et al. (2015)).

the most important change in the background geochemical conditions is the increase of pH caused by the dissolution of grout material).

In the model of Granizo and Missana (2006), the pH-dependent charge at the surface of the oxides is given by the following protonation/deprotonation reactions and related constants:

$$SOH_2^+ \leftrightarrow SOH + H^+ \quad K_{a1} \tag{1}$$

$$SOH \leftrightarrow SO^- + H^+ \quad K_{a2} \tag{2}$$

while cesium sorption onto the surface of the oxides is given by the following two reactions:

$$SOH + Cs^+ \leftrightarrow SOHCs^+ \quad K_{c2} \tag{3}$$

$$SOH + Cs^+ \leftrightarrow SOCs + H^+ \quad K_c \tag{4}$$

The values of the different surface complexation constants are listed in Table 3. The constant of reaction (4) was increased to amplify the pH dependency of cesium sorption. The number of sites considered is $2.16 \times 10^{-5}$ mol/L.

Prior to the transport simulations, we carried out two batch calculations: one with the initial water of the GC model (i.e. the groundwater type used in the shallow part of the GC domain) and the other with a high pH groundwater representative of extreme hyper-alkaline conditions. In these batch calculations, trace concentration of cesium is added to the solution and the resulting aqueous composition is equilibrated with the sorption sites. The resulting dimensionless distribution coefficients, computed as $K_d^* = F^*/C$ (–), with $F^*$ (mol/L) being the mass of radionuclide retained in the solid phase, expressed relative to a liter of water, and $C$ (mol/L) the aqueous concentration of the radionuclide, show that, when pH has nearly neutral values (i.e. initial conditions outside the grouted area of the GC model; pH=7.4), cesium is barely retarded ($K_d^* = 1.3$) whereas, when (and if) the radionuclide is overtaken by the hyper-alkaline plume (pH=10.7), the retardation increases dramatically ($K_d^* = 65$).

In MARFA, radionuclide transport simulations are usually carried out along a set of fixed pre-defined transport pathways (as in Section 3). However, the code includes an alternative option that consists in routing particles through a node network that is derived from the underlying groundwater flow field (see Appendix A). Here, we used this option and performed the MARFA calculations over a sub-domain of the GC model, which is composed of 2,506,336 cells and encompasses parts of the access tunnel (see Fig. 8). The routing information was taken from the results of the hydrogeological model (DarcyTools).

**Table 3**
Surface complexation constants.

| | |
|---|---|
| $\log K_{a1}$ | 5.10 |
| $\log K_{a2}$ | −9.10 |
| $\log K_{c2}$ | 1.05 |
| $\log K_c$ | −2.50 |

A source location for the radionuclides was arbitrarily selected in the upper part of the GC domain and close to the grouted cells. Fig. 9 shows the source location and the high pH plume at different times (note that all the radionuclides were released at time 0). After a few years from the beginning of the simulations, the source location is overtaken by the hyper-alkaline plume. After more than 3000 years, as a result of dilution and the buffering effect of secondary minerals, the plume retreats and the pH values, at the source location, decrease below 10.

Using the aforementioned radionuclide sorption model and the methodology described in Section 2, $K_d$ values were computed for every grid cell and at each PFLOTRAN output time. This information was then processed and provided to MARFA as input for the radionuclide transport calculation.

The cesium breakthrough curve computed by MARFA is shown in Fig. 10. For the sake of comparison, an additional MARFA simulation was carried out, where the distribution coefficient was kept constant equal to the value computed with the initial background geochemical conditions (i.e. groundwater with pH near neutral values).

The breakthrough curve computed using a constant $K_d$ value has a bimodal shape, with the first peak having a much higher concentration. The reason for this is to be found in the underlying heterogeneous conductivity field (Fig. 6), which is characterized by some well connected patterns along which most of the injected mass is transported (first peak; ~100 years). Part of the mass moves, however, through less connected patterns and exits the domain later (second peak; ~2, 000 years). All the released radionuclides have exited the domain at ~5, 700 years. When the evolution of background geochemistry and its influence on the cesium retention processes is taken into account, the breakthrough curve is dramatically shifted to later times, with the first peak scaling at ~2, 000 years and with all the mass exiting the domain at ~26, 000 years. This curve shows a much larger spread, which can be explained by the mutual interplay between physical heterogeneity and the changing geochemical conditions. Those radionuclides that move along “slow” paths are quickly overtaken by the perturbation and are then strongly retarded. Other radionuclides move along better connected pathways and thus can travel longer distances before being reached by the hyper-alkaline plume. The overall effect of this is that the breakthrough curve is “stretched” and the resulting peak concentration is 1.5 orders of magnitude lower than for the constant $K_d$ case.

The iFM calculation used to generate the $K_d$ data set for the considered sub-domain (~2.5 M cells) runs in 96 h on a standard desktop computer. However, much of this workload was used to open, handle and retrieve the geochemical information from the GC model. In fact, the 15 parameters used to define the background geochemical conditions in iFM (i.e. 13 aqueous species plus pH and Eh) are stored in separate hdf files. The size of each of these files is 35 GB and they contain all the information computed by PFLOTRAN at 40 time steps (i.e. from 0 to 20,000 years) and for the whole GC domain (~100 M cells). It turns out that the effective time taken by the iFM calculation is much less. Moreover, it is worthwhile noting that once the sorption model is defined, the iFM calculation needs to be run only once and the same results can be used by MARFA to solve different variant cases or sensitivity simulations.

The results of this application case demonstrate that the proposed modelling approach constitutes an appealing framework that, on the one hand, allows for the efficient solution of radionuclide transport calculations and, on the other hand, explicitly accounts for the influence that the evolving background

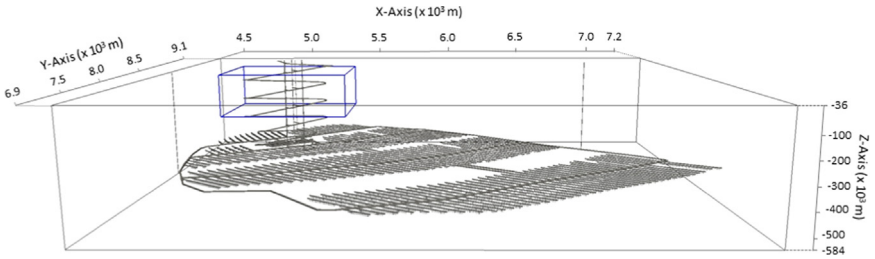


**Fig. 8.** View of the GC domain (gray box) and the sub-domain used in the iFM simulation.

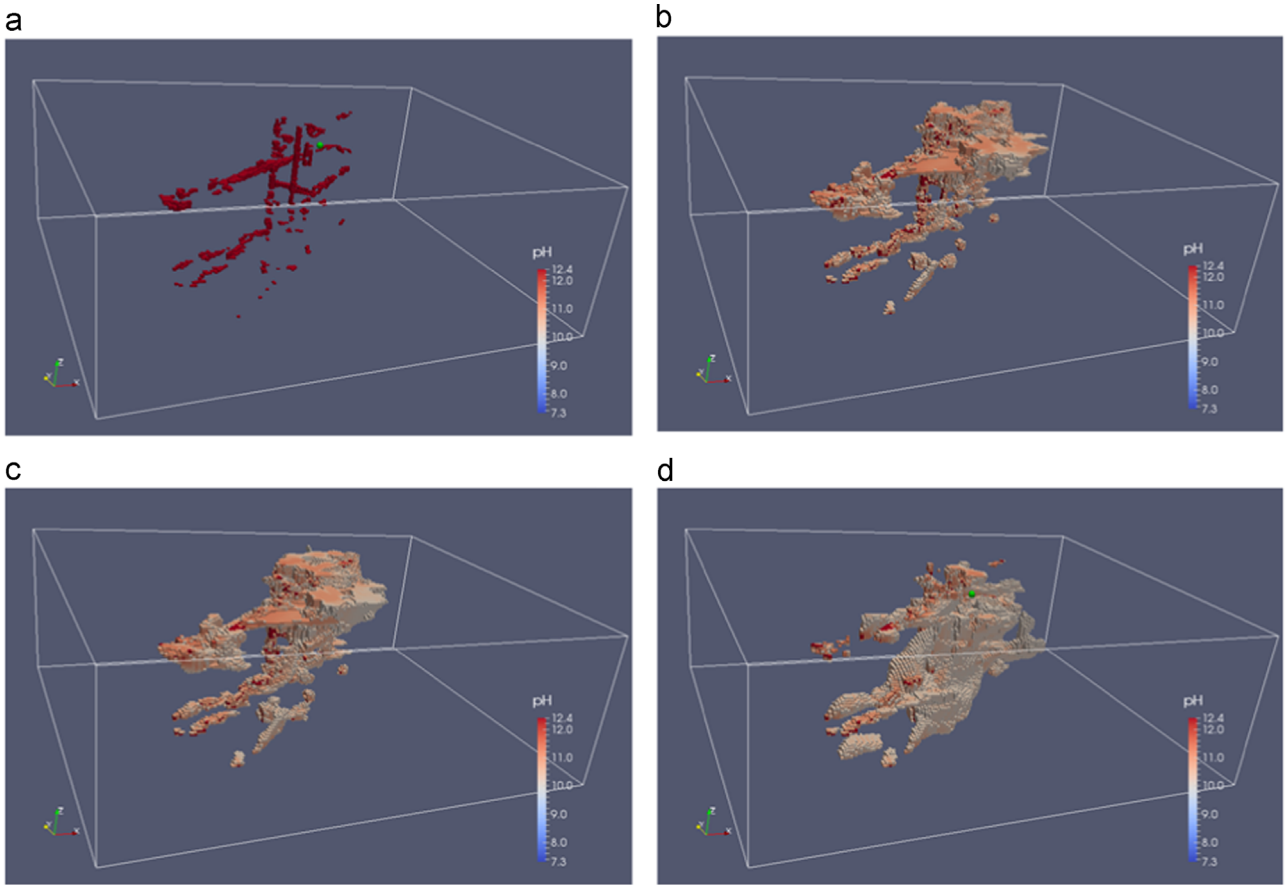


**Fig. 9.** High pH plume (pH > 10) (a) at the beginning of the simulation and at time (b) 50 years, (c) 500 years and (d) 4000 years. The box indicates the limits of the sub-domain and the green sphere indicates the source location used in the MARFA calculations. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

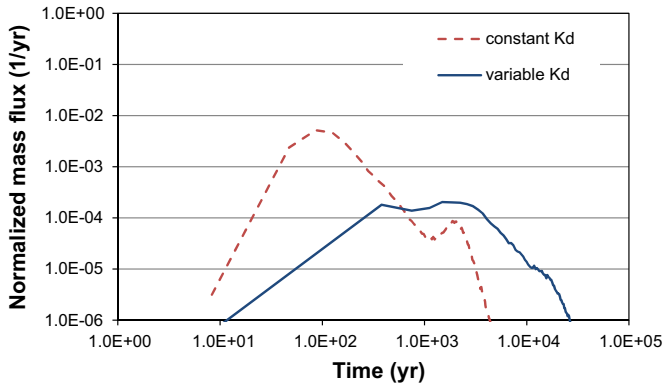


**Fig. 10.** Cesium breakthrough curves at the boundary of the considered GC sub-domain computed by MARFA with (i) constant $K_d$ equal to the value computed for the initial GC groundwater (i.e. pH near neutral values) (dotted red line) and (ii) variable $K_d$ values (continuous blue line). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

geochemical conditions have on the radionuclide retention properties.

## 5. Summary and conclusions

We proposed and tested a novel methodology for the dynamic update of the $K_d$ values used in time-domain particle tracking simulations for radionuclide transport. The methodology was coded in a python script denoted as iFM (interface to MARFA) and provides input to the time domain particle tracking code Migration Analysis of Radionuclides in the Far Field (MARFA) (Painter et al., 2008; Painter and Mancillas, 2013).

The proposed approach was tested against synthetic problems that mimic the release of strontium from a release source and its migration along a single or a set of multiple fixed trajectories. An exchanger, consisting of three different sorption sites, was considered. Both problems (i.e. single and multiple streamlines) were

solved using iFM+MARFA and also by an independent solution based on a mechanistic fully coupled reactive transport model. In both problems, the two solutions were in good agreement with some minor differences, which are attributable to binning of the $K_d$ values, the numerical dispersion of the independent calculations, MARFA's algorithm for reconstructing instantaneous breakthrough, and the Monte Carlo nature of MARFA's solution algorithm.

In the second part of the paper, iFM was run over a sub-domain (~2.5 M cells) of an existing "big" reactive transport model. This model studies the formation of an hyper-alkaline plume as a result of the dissolution of the grout used during the construction of the future deep geological repository at Forsmark (Sweden). Cesium and a model for cesium sorption onto magnetite (Granizo and Missana, 2006) were selected. The results of the radionuclide transport simulations, which were carried out with iFM+MARFA, showed the clear signature of the effect of the growing pH plume on cesium sorption. In fact, the resulting breakthrough curve is retarded and stretched compared to that computed using a constant $K_d$ value. Moreover, a simple analysis of the computational costs required by this exercise demonstrated the efficiency of the proposed approach when applied over large-scale realistic radionuclide transport problems.

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## Appendix A. MARFA: processes and conceptualizations

Radionuclide migration in fractured rock is the net result of advection and dispersion in heterogeneous flow fields, diffusion into stagnant zones in the rock matrix, and sorption on fracture surfaces and in the rock matrix. The traditional approach to modeling that combination of processes is to use finite-difference, finite-element, or Laplace-transform based approaches to numerically solve the partial differential equations representing mass conservation. When flow in the fractures is represented using highly detailed discrete fracture network simulations (see Fig. 6), those traditional solution methods become numerically challenging. Dozens of radionuclides linked through decay chains are typically of interest. Some of these radionuclides are highly mobile and interact only weakly with the rock matrix while others are strongly sorbing and migrate very slowly. Moreover, the flow fields extracted from highly detailed discrete fractured rock simulations typically have a very large range of flow velocities. Thus, small time steps and a highly resolved spatial grids are required to resolve transport of mobile radionuclides in localized high velocity zones, while long simulation times may be needed to represent the fate of slowly migrating and long-lived radionuclides. Moreover, SAs typically include formal uncertainty quantification, which may require thousands of realizations with different physical parameters sampled from uncertainty distributions and makes solution robustness critical.

The time-domain particle tracking method (Painter et al., 2008) was developed to meet the numerical efficiency and solution robustness challenges of representing radionuclide transport in SAs for radioactive waste disposal systems in fractured rock. In the time-domain particle tracking method implemented in MARFA, particles representing packets of radionuclide mass are moved on segmented transport pathways extracted from a solution to groundwater flow. Particles are advanced along each pathway using deterministic spatial displacements and random transit times for each step. The residence times for particles are based on analytical solutions to the transport equations in simplified scenarios. The composite solution procedure is formally a semi-analytical Monte Carlo solution to the radionuclide transport equations (Painter et al., 2008).

Testing and experience with the code demonstrate that MARFA is computationally efficient and extremely robust. Advection, longitudinal dispersion, diffusion into a matrix of limited or unlimited extent, equilibrium sorption on the matrix and on fracture surfaces, decay, and in-growth are represented. MARFA supports full spatial variability for all pathway properties, decay chains of any length, and full temporal variability in radionuclide source strength. The raw output of the code is particle arrival times at the pathway endpoints. A post-processing step then converts those arrival times into radionuclide mass discharge rates (breakthrough).

Two new variants of MARFA were created to accommodate fully transient geochemical conditions. It is important to note that two branches of the MARFA code exist. These two branches use different conceptualizations of the transport pathways. The new variants of MARFA are based on these two branches and use identical conceptualizations of $K_d$ variations.

In the first branch, the transport pathways are fixed in space. The groundwater speed on the pathway may vary according to pre-defined flow periods, but the spatial trajectory of each pathway is fixed. The variant of this branch has been used in the verification exercises of Section 3.

The second branch, discussed in Section 4 in this paper, allows for greater flexibility in the flow direction.

Previous versions of MARFA accommodated a limited degree of variability in $K_d$. Specifically, the spatial domain of interest was subdivided into rock types, where each rock type had a single $K_d$ for each radioelement of interest. The time period of interest was subdivided into flow periods with steady $K_d$'s and velocity within each flow period. At the time of a flow change, $K_d$ and transport velocity changed everywhere in the computational domain of interest. In the new versions created for this work, that piecewise steady approximation was retained for flow, but greater flexibility was introduced for $K_d$'s. Specifically, in the new versions, each rock type has an associated set of geochemical "states". These states are binned or discretized versions of the range of possible $K_d$ values experienced within the rocktype through the entire simulations. Each position on the transport pathway is then assigned a time sequence of states. The geochemical states ($K_d$ bins) and the sequence of states visited are calculated here by iFM and stored in two separate ASCII files: *kdbin.dat* and *kdhistory.dat* (see also Fig. 1).

## Appendix B. Supplementary data

The iFM source code along with the input files of the "single trajectory" verification case (Section 3.2) is provided as supplementary material. MARFA can be requested via email to marfacode@gmail.com.

Supplementary data associated with this paper can be found in the online version at http://dx.doi.org/10.1016/j.cageo.2015.10.005.

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