CROCK

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Results of the benchmark exercise

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Objective

The objective of this WP is to apply the outcome of other WPs to the application in the Safety Assessment, thereby decreasing the PA uncertainty and providing improvements for future site characterizations.

Scope of the Benchmark exercise

This benchmark exercise aims at assessing the potential release of a set of radionuclides at repository depth and the related migration and discharge at the surface.

It is worthwhile stressing that the different partners of this WP will focus on the evaluation of different retention processes. In fact, if on the one hand Amphos 21 will provide an integrated "overview" of the fracture-matrix interaction processes, the modelling work of KEMAKTA will be focused on the evaluation of the matrix retardation processes while the focal point of VTT will be to provide effective sorption properties based on the results of the molecular models performed in WP4.

Set-up of the benchmark exercise

1. Streamline delineation

The conceptual model assumes the release of the set of radionuclides from a number of deposition holes located in a deep geological repository.

First, a set of discharge streamlines (from the canister to the repository) has been delineated. This has been done as follows

- The Darcy's velocity field has been borrowed from the regional hydrogeological model of Olkiluoto (Löfman et al., 2012). A random component has been added to the velocity vector in order to make the exercise absolutely general and to avoid any implicit reference to the case of Olkiluoto.

- 3959 particles are injected in correspondence of the hypothetical location of a same number of deposition holes.

- The particles are tracked to the surface using the random walk particle tracking code RW3D-MT (Fernández-García et al., 2005).

The ensemble of streamlines is shown in Figure 1 and the related travel time histogram is shown in Figure 2.
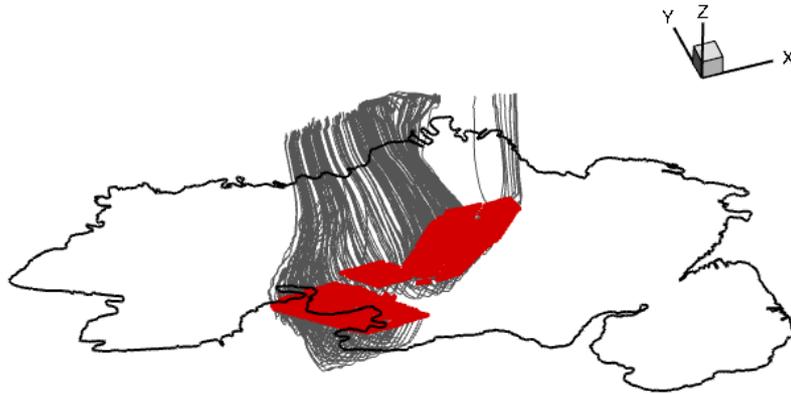

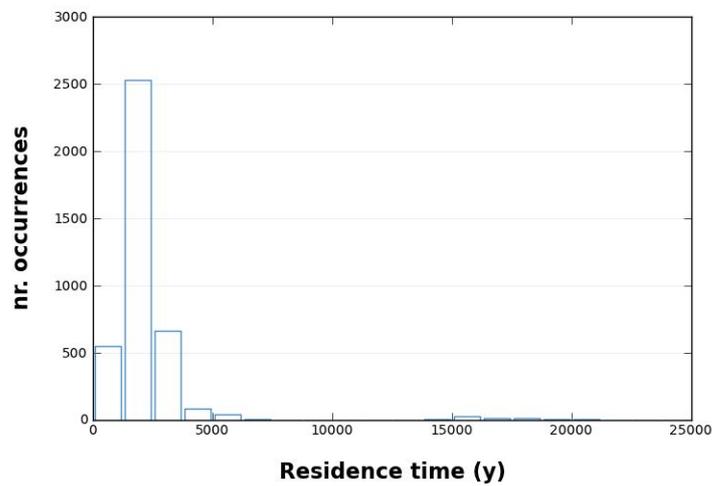**Figure 1** set of 3960 particles that delineates streamlines from the repository to the surface

Figure 2 Histogram of travel times for the 3960 injected particles.

2. Geochemical conditions

The capacity of the subsurface system to retain radionuclides, mainly via sorption or precipitation, strongly depends on the pH and redox state of the groundwater. Both parameters, together with the water composition, control the speciation of the radionuclides and the stability of the mineral phases that are able to retain them. Nevertheless, in this model set-up, no specification is provided about the redox control system. In fact, the goal of the exercise is precisely to leave liberty to each modelling team and then to test the implications of the different assumptions made by each of them.

A representative groundwater composition has been chosen (**Table 1**). This proposed groundwater is a mildly reducing water representative of the average hydrochemical conditions that are found at repository depth in a typical Fennoscandian site.

Table 1 Initial groundwater composition.

	Initial porewater
pH	6.83
Eh (mV/l)	-2.63
$[Cl]_{total}$	1.01×10^{-1}
$[S]_{total}$	2.21×10^{-3}
$[Si]_{total}$	5.63×10^{-4}
$[PO_4^{3-}]_{total}$	6.46×10^{-8}
$[Na]_{total}$	6.13×10^{-2}
$[K]_{total}$	8.00×10^{-4}
$[Ca]_{total}$	1.83×10^{-2}
$[Mg]_{total}$	1.83×10^{-2}
$[Sr]_{total}$	6.95×10^{-5}
$[Ba]_{total}$	4.36×10^{-7}
$[C]_{total}$	4.82×10^{-3}
$[Fe]_{total}$	5.80×10^{-5}
$[U]_{total}$	3.90×10^{-9}
$[Cs]_{total}$	3.65×10^{-9}
$[NH_4^+]_{total}$	7.28×10^{-5}

It is assumed that the open fractures of this synthetic system are mainly populated by calcite, hematite and clay minerals and that they have been observed in 32%, 24% and 11% of the mapped fractures. The average mineral thickness is specified in **Table 2**.

Table 2 Average mineral thickness

Mineral	Average thickness (mm)
Calcite	3.40×10^{-2}
Clay minerals	8.20×10^{-2}
Hematite	1.00×10^{-2}

The average fracture aperture as well as the parameters related to matrix diffusion is summarized in Figure 3 and Table 3.
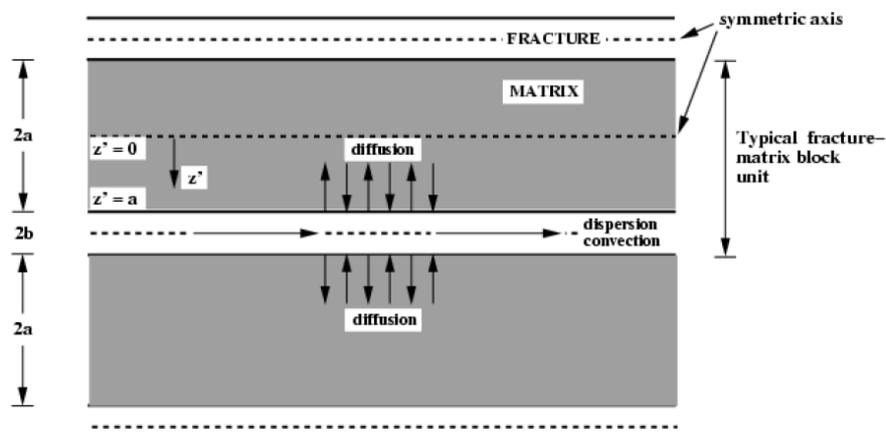

Figure 3 Parallel fracture model used to describe the fractured system (modified from Löfman et al., 2010).

Table 3 Parameters and values used for the DP model parameterization.

Symbol	Parameter	Value
a	Half matrix thickness	4.15 m
b	Half fracture aperture	$1.83 \cdot 10^{-4}$ m
D_0	Molecular diffusion coefficient in the water	$1.0 \cdot 10^{-9}$ m^2/s
ϕ_{im}	Matrix porosity	$1.0 \cdot 10^{-4}$ (-)

Different fractures apertures will be considered in order to test different ranges of F-quotients.

Methodological approach and ongoing work

The modelling work of the different partners of WP5 is still ongoing and a full account of the results will be presented in the Final workshop of the Crock project that will be held in Karlsruhe, next May 2013.

AMPHOS 21

Amphos 21 is running the different cases of the benchmark exercise using the methodology called FASTREACT (FrAmework for Stochastic REACtive Transport). The methodology consists in coupling a set of 1D reactive transport simulations with one or multiple random-walk particle tracking realizations (see Figure 4; for the details of the methodology the reader is referred to Trinchero et al., 2010).
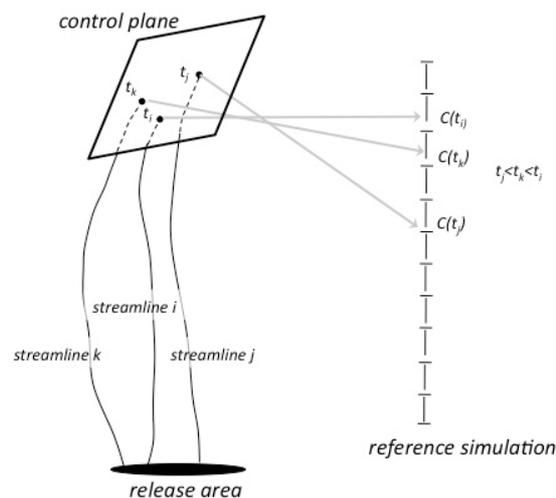

Figure 4 Illustrative sketch of the FASTREACT methodology

Preliminary calculations have been carried out and the results are summarized in the next section. These simulations, which focus on the evaluation of the transport of three radionuclides (strontium, caesium, and uranium) as well as a conservative tracer (here assimilated to HTO) will be improved in terms of better and more reliable representation of the retention processes. Sensitivity analysis to the different key parameters will be carried out. Also, if possible, the model will be extended in order to account for other radionuclides of interest (e.g. Europium and Iodine).

KEMAKTA

Kemakta's immediate goal is to use a fully coupled reactive transport code in an attempt to reproduce the results already obtained using the simplified decoupled major ion chemistry approximation modelling approach for the solutes Sr^{2+}, Cs^+, Ra^{2+} (documented in the S&T contribution to the 1st annual workshop proceedings (Crawford, 2012)). This should demonstrate whether the approximation can be used for speeding up reactive transport calculations involving radionuclides at very dilute, trace concentrations. An additional set of full reactive transport calculations will also be performed for the benchmark case involving constant groundwater chemistry and a set of discrete F-factors representing a typical range of hydrodynamic transport resistances encountered in PA calculations. Since the groundwater chemistry is defined to be temporally and spatially invariant in the benchmark case, the breakthrough curves for the reactive transport simulations are not expected to differ from the analytical solution for transport of a dilute solute with constant K_d for the specified groundwater chemistry. Reasons for any deviations from this expected behaviour will be investigated. Depending on whether a viable Surface Complexation Model (SCM) for the granite matrix rock becomes available from WP4 in time, the calculations may be extended to some analogous cases involving the surface complexers, Ni and Eu.

VTT

Objective of the VTT's work in the CROCK is to facilitate assessment of the Kd values to different conditions and different scales and to evaluate uncertainties that are connected to the assessment of the Kd values. The focus of the work is on radionuclides and conditions that are relevant for the KBS3 type repository in the crystalline rock. The benchmark exercise demonstrates application of the scaling procedure for a realistic PA application. In addition, the benchmarking exercise enables comparison between alternative modelling approaches of the other modelling teams.

The main objective of the VTT's work within the framework of this WP is on the upscaling process. This means that the set of modelled radionuclides will be limited to nuclides that are most appropriate to demonstrate all steps of the upscaling.

The modelling is based on upscaled sorption properties for three different scales: molecular level (less than 100 atoms), surface complexation and a single fracture scale (partial flow paths of the benchmarking exercise). Finally, transport properties are also applied in the PA modelling over the entire length of the flow paths in the benchmark exercise. The approach can be summarised by four steps:

- Molecular level computations. This modelling is carried out for a representative rock mineral. The aim is to simulate surface reactions on molecular level. Results of this step will be applied in the surface complexation modelling.

- Surface complexation modelling. This modelling step gives the applicable Kd-values for the modelled radionuclide in the selected geochemical conditions. For example, representing properties of the initial fracture water and pore water of the benchmarking exercise.

- Reactive transport modelling. Transport of the selected radionuclide is modelled by a surface reaction model for simplified flow paths and rock matrix geometries.

- Application of PA migration model using flow paths specified by the benchmarking exercise and results from the previous steps.

The benchmarking simulations are carried out using a PA migration model (FTRANS, GoldSim or MARFA). Flow paths are conceptualised as flow channels on fracture planes surrounded by the porous rock matrix. Flow is possible only along the flow channel and the pore space in the rock matrix is immobile. A representative set of the flow paths from the definition of the benchmark exercise are used in the simulations. Flow paths are simulated separately and hydrodynamic control of retention (the F-quotient or WL/Q) for each path is deduced from the fracture aperture and the water residence time. Fracture coating could be included to some of the simulations as an additional immobile layer of the rock matrix. Simulation of the radionuclide migration is repeated for alternative upscaled Kd's representing the bounding geochemical conditions along the flow paths.

Some illustrative results

For the sake of brevity, in this chapter we summarize some of the preliminary results of the radionuclide transport calculations carried out by Amphos 21. The aim of this is to provide an illustrative picture of the kinds of results produced in this WP rather than to present a full account of the outcome of the modelling exercise. An exhaustive discussion on the different modelling results obtained by the different partners will be presented in the final workshop of the CROCK project that will be held in Karlsruhe, next May 2013. In the same workshop, the three partners will present a joint S&T contribution with a detailed comparison of the different modelling results.

As mentioned above, these preliminary calculations, which have been carried out using the methodology FASTREACT (see previous section) have focused on the evaluation of the transport of three radionuclides, namely strontium, caesium, and uranium as well as a conservative tracer (here assimilated to HTO). A pulse-like release of these four radionuclides is assumed to occur at repository depth.
The different retention processes used in the modelling work are summarized next.

Strontium

For the case of strontium, the two main processes considered as possible retention mechanisms are the co-precipitation of Sr with calcite, forming a solid solution, and the sorption of Sr onto clays.
In the numerical modelling, the co-precipitation of strontium with calcite will take place as long as saturation is reached. Sr sorption onto clays is modelled using the thermodynamic constants reported for illite. In other words, illite has been selected as a proxy mineral phase to represent the behaviour of the clay minerals in the model.

Caesium

Similarly to Strontium, clay minerals are strong sinks for caesium. Therefore, in the numerical model, the sorption of caesium onto illite is the only retention process considered. In this case too illite is selected as a mineral phase representing the behaviour of all clay minerals in the fractures.

Uranium

In the reactive transport simulations, a set of minerals has been selected as possible solubility-limiting phases of aqueous uranium. For U(VI), a hydrated amorphous phase ($UO_2 \cdot 2H_2O$) has been used instead of a crystalline phase (e.g. uraninite). Also, schoepite and uranophane are allowed to precipitate if the solution becomes oversaturated with any of these phases.

The thermodynamic database used for aqueous speciation is the SKB-TDB (Hummel et al. 2002) with substantial modifications as reported in Duro et al. (2006), Grivé et al. (2008) and Arcos and Piqué (2009).

Bradbury and Baeyens (2000) proposed a model of cation exchange for illite which is here considered as representative for all the clay minerals, considering three types of sites ("planar", "type II" and "Frayed Edge Sites"). The total concentration of sites in illite, the model clay mineral in this study, is kept constant during the reactive transport simulations since it is assumed that this mineral phase does not dissolve nor precipitate in the environmental conditions considered in the model. A cation exchange capacity (CEC) value of 225 meq/kg has been considered for illite (Baeyens and Bradbury, 2004), and according to this CEC, the concentration of cation exchange sites (CES) in the fracture-filling is set as follows:

- CEC = 225 meq/kg = 0.225 eq/kg = 0.225 mol/kg (exchange species is a monovalent X^-)
- $[CES]$ = 0.225 mol/kg CEC x 0.02 kg/L$_{water}$ = 0.0045 mol/L$_{water}$

The initial exchanger composition has been considered to be in equilibrium with the reference groundwater.

Table 4 Cation exchange reactions and their corresponding Gaines-Thomas selectivity coefficients for illite

Reaction	Log K (25°C)	Reference
Planar sites		
$X^- + Na^+ \leftrightarrow NaX$	0.0	(1)
$X^- + K^+ \leftrightarrow KX$	1.1	(1)
$X^- + Cs^+ \leftrightarrow CsX$	1.6	(1)
$2X^- + Sr^{2+} \leftrightarrow SrX_2$	1.13	(2)
$2X^- + Ca^{2+} \leftrightarrow CaX_2$	1.13	(2)
$2X^- + Ba^{2+} \leftrightarrow BaX_2$	1.13	(2)
$2X^- + Mg^{2+} \leftrightarrow MgX_2$	1.13 [a]	
$2X^- + Ra^{2+} \leftrightarrow RaX_2$	1.13 [a]	
$2X^- + UO_2^{2+} \leftrightarrow UO_2X_2$	0.65	(3)
Type II sites		
$X^{II-} + Na^+ \leftrightarrow NaX^{II}$	0.0	(1)
$X^{II-} + K^+ \leftrightarrow KX^{II}$	2.1	(1)
$X^{II-} + Cs^+ \leftrightarrow CsX^{II}$	3.6	(1)
FES		
$X^{FES-} + Na^+ \leftrightarrow NaX^{FES}$	0.0	(1)
$X^{FES-} + K^+ \leftrightarrow KX^{FES}$	2.4	(1)
$X^{FES-} + Cs^+ \leftrightarrow CsX^{FES}$	7	(1)
$X^{FES-} + NH_4^+ \leftrightarrow NH_4X^{FES}$	3.5	(1)
(1) /Bradbury and Baeyens 2000/. (2) /Brouwer et al. 1983/. (3) /Bradbury and Baeyens 2009/.		
(a) Value assumed, considering an equal sorption behaviour for all the alkaline earth elements.		

Table 5 Calculated initial composition of the cation exchange sites in illite

Site	$mol \cdot L_{water}^{-1}$
Planar sites	
CaX_2	1.19×10^{-3}
NaX	4.72×10^{-4}
MgX_2	3.29×10^{-4}
KX	7.54×10^{-5}
SrX_2	3.76×10^{-15}
BaX_2	2.62×10^{-8}
CsX	2.95×10^{-14}
RaX_2	5.89×10^{-15}
UO_2X_2	1.17×10^{-15}
Type II sites	
KX^{II}	5.53×10^{-4}
NaX^{II}	3.47×10^{-4}
CsX^{II}	2.16×10^{-12}
FES	
NH_4X^{FES}	4.96×10^{-6}
KX^{FES}	4.21×10^{-6}
NaX^{FES}	1.32×10^{-6}
CsX^{FES}	2.07×10^{-11}

The calculations have been carried out using both a single and a dual porosity approach. In the former (denoted as Model A), transport and reactions occurs only in the fractures while in the latter (denoted as Model B) mass exchange occurs between the mobile domain (the fractures) and the matrix. The dual porosity approach has been implemented using a first-order exchange approximation (van Genuchten 1985) and the matrix has been considered as non-reactive.

Figure 5 shows the normalized breakthrough curves of HTO for the two considered models. It is worthwhile noting that in model A the breakthrough curve reflects the distribution of the ensemble of trajectories (Figure 2), with a sharp arrival peak followed by a fast decrease of concentration. In model B, the effect of the matrix is evident as the breakthrough curve shows a lower peak value and a long tail.
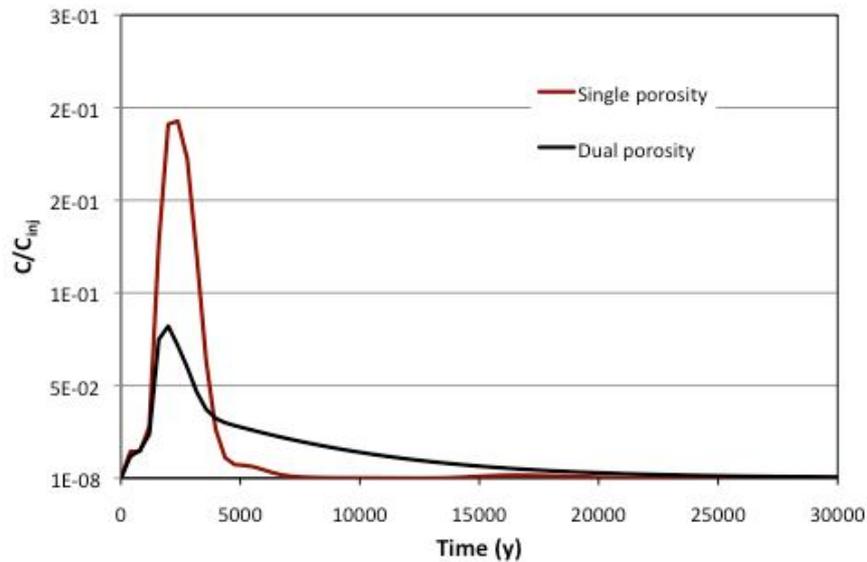
Figure 5 Breakthrough curve of HTO for the single porosity model (red line) and the dual porosity model (black line). The curves are normalized by the injection concentration.

Figure 6 and 7 show the breakthrough curves of uranium and strontium respectively. Their qualitative shapes are similar to those of the conservative simulations although the different retention processes implemented in the model result in an average retardation factor of 2.4 and 2.0 respectively.
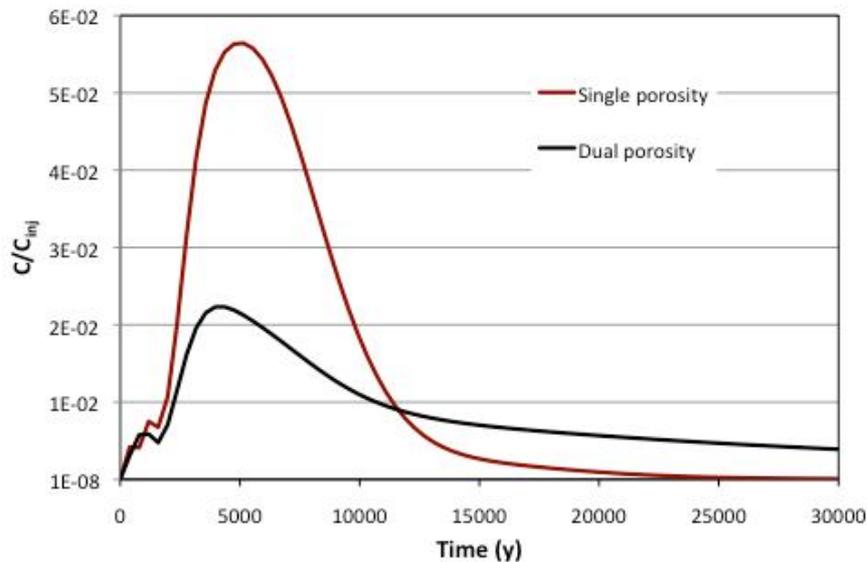

Figure 6 Breakthrough curve of uranium for the single porosity model (red line) and the dual porosity model (black line). The curves are normalized by the injection concentration.
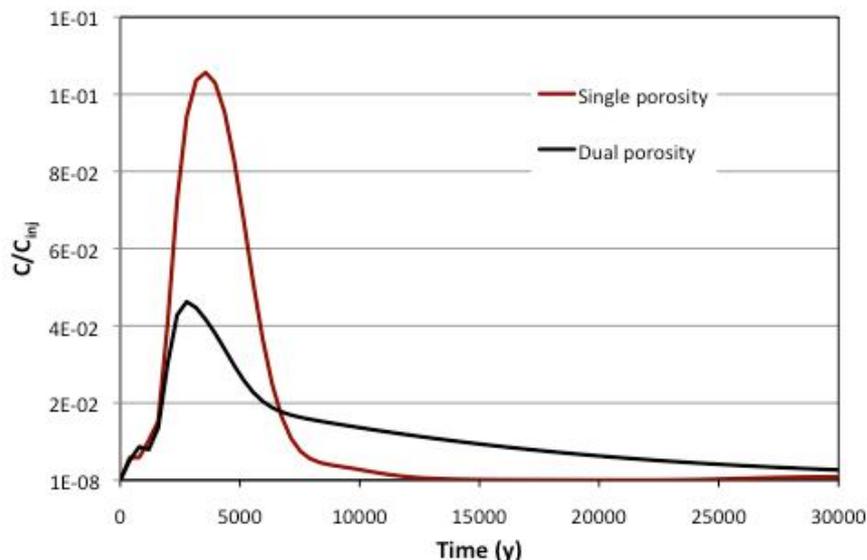
Figure 7 Breakthrough curve of Strontium for the single porosity model (red line) and the dual porosity model (black line). The curves are normalized by the injection concentration.

Figure 8 shows the breakthrough curve of caesium. Due to convergence problems, only the results of the single porosity model are available, so far. It is evident that the isotope is strongly sorbed onto the available clay minerals (in particular, illite) and the rise of concentration is extremely slow during the considered time frame.
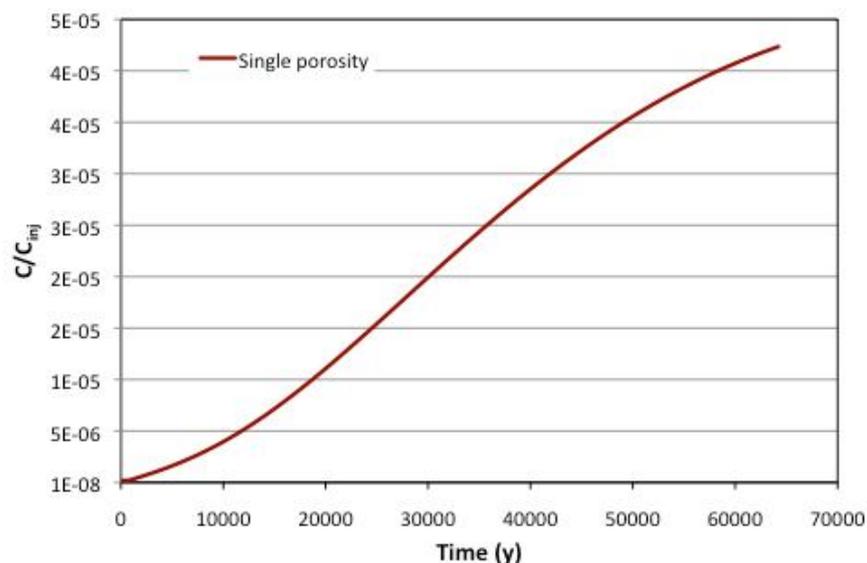

Figure 8 Breakthrough curve of caesium for the single porosity model. The curve is normalized by the injection concentration.

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