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Authors

Orucoglu, E
Van Den Akker, BP
Ahn, J

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Effects of depth on transport of ^{129}I in crystalline rock

Esra Orucoglu*, Bret P. van den Akker, Joonhong Ahn

Department of Nuclear Engineering, University of California at Berkeley, Berkeley, CA 94720-1730, USA

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ABSTRACT

In the present paper, a model for the transport of iodine through fractures in granitic rock has been developed by taking into account the variation of parameters with depth in order to investigate the effects of depth on repository performance. First, the evolution of groundwater chemistry with depth has been modeled by considering the physical and chemical conditions that vary with depth. Second, iodine–water interactions and iodine–rock interactions under groundwater–chemistry evolution with depth in crystalline rocks have been modeled using PHREEQC, with which the distribution coefficients of iodine have been numerically evaluated as a function of depth. These values and other depth-dependent parameters such as fracture aperture, groundwater velocity, and diffusion coefficients have been used in the iodine transport simulation to observe differences in the iodine concentration in the water from repositories located at 500 and 1000 m depths. The results show that iodine stays within the vicinity of the repository if it is disposed of at a greater depth. The main reason is that the retention effect of matrix diffusion increases and relative contribution of advection along fractures decreases at depth due to the cubic law for the water flow velocity in fractures.

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1. Introduction

1.1. Scope and objective of the present study

Iodine 129 has high fission yields in ^{235}U and ^{239}Pu atoms, 0.6% and 1.6% respectively, a long physical half-life (1.57×10^7 y), and high potential mobility in soil (Söderlund et al., 2011; Bate and Stokely, 1980). It has been one of key issues in the long-term radiological safety for geological disposal of intermediate and high-level radioactive wastes, including spent nuclear fuel (Grambow, 2008; Tigeras et al., 2011). Additionally, iodine exhibits complex geochemical behavior and its chemical speciation determines its transport behavior in aqueous environments (Johnson, 2003). For reliable performance assessment for the geological disposal of such wastes, which are likely to be disposed of at depths of a few hundred meters or greater, it is imperative to determine proper values of parameters that are included in the transport models, such as the pore velocity of groundwater, dispersion coefficients, and sorption distribution coefficients. Because these transport parameters are dependent on temperature and pressure, their values vary along the transport pathway. It is of interest to investigate iodine transportation by taking into account the depth dependency of

the transport parameters. In this paper, we aim at the development of an iodine transport model with depth-dependent parameters in order to observe the effects of depth on the performance of the repository system.

For this purpose, following the conventional approach for performance assessment, the present study has been carried out in three stages: (1) development of mathematical formulation and computational tool for a transport equation with depth dependent parameters, (2) modeling and/or formulation of parameters included in the governing equation as functions of depth, and (3) numerical exploration of iodine transport.

The first stage has been achieved by utilizing the model and code, TTBX, previously developed by van den Akker and Ahn (2014), for a multi-segmented 1-dimensional pathway for a multiple-member decay chain. The variation of transport parameters along the pathway has been accommodated by segmenting the pathway and assigning average values to each of these segments.

For the second stage, depth-dependency has been determined by literature for basic physical properties, such as the density and viscosity of water, and the iodine diffusion coefficient. The depth-dependent water velocity in rock fractures has been formulated by considering the dependence of the fracture aperture on depth (see Section 6). The major task in the second stage, however, has been the evaluation of the sorption distribution coefficient (Kd) of iodine in varying geochemical conditions due to changes in

* Corresponding author. Address: Faculty of Mines, Istanbul Technical University, TR-34469 Maslak, Istanbul, Turkey. Tel.: +90 212 285 6183; fax: +90 212 285 6131.
E-mail address: orucoglu@itu.edu.tr (E. Orucoglu).

temperature and existing minerals.¹ Because different species exhibit different chemical reactions with the host rock and groundwater, first the evolution of groundwater composition has been modeled by considering the depth dependency of such basic parameters as temperature. Then, including the effects of chemical speciation and sorption equilibrium modeling, the sorption distribution coefficients (K_d) of iodine species at various depths were determined for granitic rock and fracture-filling materials. The geochemical modeling code, PHREEQC (version 3.0.1.7), has been used in modeling radionuclide-groundwater-rock interaction to evaluate the sorption distribution coefficients as a function of depth.

In the third stage, a parametric study was performed to observe the effects of repository depth on the retention of iodine within geological formations. The results obtained from this study are expected to contribute to the enhanced reliability of performance assessments for geological disposal systems.

1.2. Previous studies

The transport of radionuclides in discrete fractures with matrix diffusion has been investigated since the 1980s, and mathematical solutions were obtained by various researchers (Neretnieks, 1980; Tang et al., 1981; Chambre et al., 1982; Sudicky and Frind, 1984). Hodgkinson and Maul (1988) developed a 1-D model for the transport of radionuclides through a single type of permeable or fractured rock using the numerical inversion of Laplace transforms. Ahn (1998) developed the Transport to Biosphere (TTB) code by combining this Hodgkinson and Maul model with a detailed source-term model. Recently, a model and an extended code (TTBX) for release and transport of radionuclides through a 1-D fractured medium have been developed by van den Akker and Ahn (2014), which accommodates a multi-segmented transport pathway through an arbitrary number of rock types for a multiple-member decay chain. A numerical illustration of the TTBX code was given for disposal of TRISO spent fuel at the Yucca Mountain Repository (van den Akker and Ahn, 2013).

For the evaluation of K_d , it is imperative to understand the speciation and chemical reactions of iodine in the aqueous environment and retardation mechanisms in geologic formations. The evaluation includes three components: (1) iodine speciation, (2) iodine sorption on rock minerals, and (3) evolution of groundwater compositions.

Palmer et al. (1985), Lengyel et al. (1993) and Gottardi (1999) modeled the iodine speciation as a function of pH. Palmer et al. (1985) studied hydrolysis of I_2 to I^- and IO_3^- experimentally at the temperature range between 3.8 and 209 °C. Obtained data were incorporated into a general computer model to simulate hydrolysis equilibrium as a function of temperature, pH and initial concentration. Based on the analysis for direct measurements of the kinetics of iodine hydrolysis at various temperatures by Eigen and Kustin (1962), and Palmer and van Eldik (1986), Lengyel et al. (1993) considered overall iodine hydrolysis reactions between pH 2 and 7, and modeled speciation as a function of pH by using a consistent set of equilibrium constants. Gottardi (1999) investigated iodine speciation for various pH. Since disproportionation to iodate proceeds rather slowly, he only considered

the fast reactions in speciation calculations. Among these three researches, only Palmer et al. (1985) used the temperature-dependent equilibrium constants and considered the iodate formation reaction in their pH-dependent speciation models.

Iodine sorption onto various minerals has been modeled using different methods. Wang et al. (2001) applied a surface complexation model based on the diffuse double-layer theory to study sorption of I^- onto cinnabar and chalcocite and sorption of IO_3^- onto hematite. Nagata et al. (2009) used the triple-layer surface complexation model (TLM) for modeling experimental results of Whitehead (1974) of iodine sorption onto hydrated ferric oxide and aluminum oxide. Whitehead (1974) investigated the effect of pH on iodine sorption onto some soil and soil components such as hydrated ferric oxide and aluminum oxide. Since no sorption onto kaolinite or montmorillonite was observed at pH 4, pH dependent sorption experiments were not conducted for these materials. It was found that sorption by ferric oxide was considerable between pH 2.5 and 5.5 but declined sharply above pH 5.5 to zero at about pH 7. The iodine sorption onto aluminum oxides at pH 5.5 to 7.5 was similar to that of ferric oxide.

A conceptual groundwater evolution model was developed by Japan Nuclear Cycle Development Institute (JNC) in the Tono uranium mine site (JNC, 2000,4), and was tested by Sasamoto et al. (2004) by applying equilibrium-based concepts of water-rock interaction for explaining observed variations in the mineralogy and hydrochemistry of the Tono mine area. They assumed that equilibrium was attained between mineral and fluid, and that homogeneous reactions determined the composition of the site-generic groundwaters. They used the PHREEQE geochemical code (Parkhurst et al., 1980) and the thermodynamic database PNC H3.0 (Yui et al., 1992), which consists of the original database included in PHREEQE and additional and revised data recommended by the OECD/NEA. In their study, the conceptual model was evaluated only for 25 °C, because all equilibrium constants were described at 25 °C, and reaction enthalpies were unavailable for many aqueous association reactions and mineral-dissolution reactions. Because the PNC H3.0 database did not include data for most clay and zeolite minerals, they did not consider these minerals in their calculations. Their model was used to evaluate groundwater composition at a single location; dependency with depth was not shown.

2. Geochemical modeling for iodine interactions with rock and water

In this section, we investigate the reaction models for iodine speciation, iodine sorption onto aluminum oxide mineral, and groundwater evolution using PHREEQC. The PHREEQC code is capable of simulating a wide range of equilibrium reactions between water and minerals, ion exchangers, surface complexes, solid solutions, and gases (Charlton and Parkhurst, 2011). Then we verify the models by comparing simulation results achieved with the PHREEQC code with results of in-situ measurements reported elsewhere. Finally, sorption distribution coefficients of iodine as a function of depth are calculated, which are used as one of input parameters for transport simulation by the TTBX code.

2.1. Iodine chemistry in water

In aquatic environments, iodine can be found in the form of iodide (I^-), iodate (IO_3^-) or organo-iodine (Wren, 2004; Hu et al., 2005). The aqueous iodine chemistry is mainly governed by hydrolysis of molecular iodine to hypiodous acid (HIO), and disproportionation of HIO, as given in reactions 1–3 in Table 1 (Tigeras et al., 2011; Bruchertseifer et al., 2003).

¹ It is well known that reactions and mass transfer of a radionuclide are dependent on various microscopic factors, such as grain size and chemical composition of the water used. Because the K_d is a macroscopic phenomenological model, it is not possible to model sorption at an arbitrary water composition or speciation rigorously. Having said this, the authors would like to note that the K_d model and K_d data are broadly used and accepted in regulatory-reviewed licensing of geological repositories, such as the current activities in Sweden and Finland demonstrate. Considering that the main objective of the present paper is to develop a performance assessment (PA) model, the authors believe that the method shown in this paper is a reasonable extension of the approach that has been adopted in various PA activities.

Table 1

Iodine reactions used in PHREEQC simulation.

Reaction	K	Temperature dependence of log K or ΔH
1) $I_2(aq) + H_2O \leftrightarrow I^- + HIO(aq) + H^+$	$5.4 \cdot 10^{-13}^a$	$-13.0056 + 0.01975 T - 1534.4835/T^b$
2) $I_2(aq) + H_2O \leftrightarrow HI_2O^- + H^+$	$1.6E-10^b$	Assumed constant
3) $3I_2(aq) + 3H_2O \leftrightarrow 5I^- + IO_3^- + 6H^+$	$1.17e-47^c$	$631.24 - 42304/T - 216.73 \log T^c$
4) $HIO \leftrightarrow H^+ + IO^-$	$2.30E-11^d$	$-526.75 - 0.08965T + 29688/T + 188.4775 \log T - 2.0468e6/T^{2c}$
5) $HI_2O^- \leftrightarrow I_2O^{2-} + H^+$	$3.3E-15^e$	Assumed constant
6) $H^+ + IO_3^- \leftrightarrow HIO_3$	$(1/0.164^f)$	$-21.589 + 657.15/T + 8.158 \cdot \log T^c$
7) $HIO(aq) + H^+ \leftrightarrow H_2IO^+$	$(1/0.045^g)$	$20.9735 - 5852.673/T^a$
8) $I_2 + I^- \leftrightarrow I_3^-$	690^c	$7.355 + 555/T - 2.575 \log T^c$
9) $2I^- \leftrightarrow I_2 + e^-$	$6.2E-20^g$	$\Delta H = 31.78 \text{ kcal/mol}^h$
10) $I_2(aq) \leftrightarrow I_2(g)$	3.32^j	$\Delta H = 9.523 \text{ kcal/mol}^h$
11) $HIO(aq) \leftrightarrow HIO(g)$	187.27^j	$\Delta H = 9.5 \text{ kcal/mol}^i$

^a Allen and Keefer (1955).^b Lengyel et al., (1993).^c Palmer et al. (1985).^d Eigen and Kustin (1962).^e Chia (1958).^f Atwater (1996).^g Calculated from redox potential $E = 0.615 \text{ V}$, Url-1.^h Wagman et al. (1965).ⁱ Lin (1981).

Under acidic and oxidizing conditions, molecular iodine is the major species, while iodide and iodate can be found together in neutral and basic solutions. At higher pH (>10) values, HOI dissociates significantly as given in reaction 4 in Table 1 and the hypoiodite ion (IO^-) is formed (Bruchertseifer et al., 2003). Molecular iodine is also in equilibrium with iodide to form the triiodide complex (I_3^-) as given in reaction 8 in Table 1, although Lin (1981) mentioned that the I_3^- concentration is negligible when the total iodine concentration is below 10^{-5} M . In this study, formation of triiodide complex is taken into account.

Tigeras et al. (2011) pointed out the other complexity of the iodine chemistry, which is due to volatile characteristics of some species (I_2 , HOI and some organoiodine species such as CH_3I) and the transfer between two phases. The volatile character of a solution is determined by its integral partition coefficient (IPC), which is the ratio of iodine species concentrations in the liquid to gas phases and is taken into consideration in this study as given in Table 1, reactions 10 and 11.

Iodine speciation is affected by temperature, pH, redox potential and existence of organic matter (Otosaka et al., 2011; Taghipour and Evans, 2002;). The uptake of iodine by organic matter cannot occur under anoxic conditions, for which essentially all the iodine is present in the iodide form (Richard and Goana, 2011). The measurements for granitic rocks at the Tono site showed that groundwater is in reducing conditions (Iwatsuki et al., 2005). Due to the low possibility of interaction between iodine and organic material at anoxic condition and existence of reducing groundwater conditions at granitic rock, the effect of organic material is not considered in this study.

The investigation of organic materials in sedimentary and granite in the Tono area showed that the concentration of organic carbon in the groundwater ranges from 0.1 to 8 mg C/l and trace elements such as I, Cs, Th, Cr and rare-elements in the groundwater are barely detectable in humic and fulvic acid (JNC, 2000,2). Future studies may investigate the effect of organic matter on iodine behavior in granitic rock environments.

As shown in Table 1, we have also collected the equilibrium constants, especially temperature-dependent equilibrium constants, from the literature (Allen and Keefer, 1955; Palmer et al., 1985; Eigen and Kustin, 1962; Chia, 1958; Lin, 1981). For reactions 9 and 10, the enthalpy changes of the reactions are calculated from the enthalpy of formation values of the species given in Wagman et al. (1965). The enthalpy change of the reaction 11 was

recommended by Lin (1981) based on their experimental results. Since the heats of reaction 2 and 5 are unknown, their equilibrium constants are taken as constant.

Based on the reactions and data shown in Table 1, iodine speciation for a solution with an iodine concentration of $10^{-4} \text{ g-atom/kg}$ at 25°C has been simulated by the PHREEQC code for various values of pH, and the results have been benchmarked against the experimental data reported in Palmer et al. (1985). The results obtained from PHREEQC with the aforementioned set of reactions and equilibrium constants were in good agreement with the results reported in Palmer et al. (1985).

2.2. Iodine sorption on rock minerals

The iodine–rock interaction has been investigated to model iodine sorption by using the diffuse double layer model (DLM), which the PHREEQC code is capable of simulating. Iodate sorption reactions are not considered, because it is observed from the PHREEQC results that iodine is the only existent species in the iodine–groundwater–rock interaction. Sorption of iodine onto amorphous aluminum oxide, which was modeled with TLM by Nagata et al. (2009), is modeled by using the DLM in this study. To apply the DLM, protonation/deprotonation constants of the mineral, iodine surface complexation constants, and surface characteristics of the mineral, such as the surface site density (site/nm^2), the specific surface area (m^2/g), and the amount of the mineral, should be known. However, there is not enough information to determine (1) protonation/deprotonation constants of amorphous aluminum oxide mineral and (2) iodine surface complexation constants from the current literature.

Mathur and Dzombak (2006) mentioned that hydrous metal oxide surfaces, such as goethite, hydrous ferric oxide, hematite, aluminum oxides, and others, might have similar surface complexation constants for ions. They compared surface complexation constants for similar surface reactions of ions on goethite and hydrous ferric oxide. The results showed close agreement of the surface complexation constants. According to their findings, they suggested that if differences among iron oxides in surface site density and surface area are taken into account, the free energy of reaction of an ion at the majority of surface hydroxyl sites is approximately constant. Additionally, linear free energy relationships (LFERs) can be used to estimate the surface-complexation constants of cations

or anions for which limited or no sorption data exists (Dzombak and Morel, 1990).

In this study, protonation/deprotonation constants for gibbsite mineral have been used for those of the amorphous aluminum oxide surface, and iodine surface complexation constants have been estimated by using LFERs as a starting point. Then, they are fitted to the experimental iodine sorption data given in Nagata et al. (2009) by tuning the values of protonation/deprotonation constants of gibbsite and iodine surface complexation constants. In Karamalidis and Dzombak (2010), the protonation and deprotonation constants for gibbsite mineral are defined as in Eqs. (1) and (2):

The fitted lines for the correlation of $\log K_1^{\text{int}}$ and $\log K_2^{\text{int}}$ with deprotonation constants ($-\log K_a$) for various anions have the following reactions and functions, respectively, for the sorption of different anions onto gibbsite given in Karamalidis and Dzombak (2010):

The deprotonation reaction of the iodine anion and related constant are given below (Weerasooriya and Wickramarathna, 1999):

By using this iodine deprotonation constant, the intrinsic constants for iodine sorption reactions are obtained by Eqs. (3) and (4) as $\log K_1^{\text{int}} = 5.20$ and $\log K_2^{\text{int}} = -2.23$.

In order to apply the surface complexation method, the total concentration of the surface sites (N_T) should also be known. This is calculated from Eq. (6), given in Karamalidis and Dzombak (2010):

$$N_T = N_S \times A_s \times C_s \times \frac{1}{N_A} \times \frac{10^{18} \text{ nm}^2}{\text{m}^2} \quad (6)$$

where N_S indicates site density (site/nm²), A_s is specific surface area (m²/g), C_s is solid concentration (g/L) and N_A is Avogadro's number (6.02×10^{23} sites/mol).

It is expected that the protonation/deprotonation constants of the amorphous aluminum oxide and the iodine surface complexation constants are similar to the values for gibbsite. To identify these constants for amorphous aluminum oxide, the experimental iodine sorption data from Nagata et al. (2009) has been used for adjustment. Nagata et al. (2009) modeled Whitehead's (1974) I⁻ adsorption experiments on amorphous aluminum oxide by using the TLM. In this study this phenomenon is modeled with the DLM by using the PHREEQC code for 3.15×10^{-6} M [I⁻] concentration in 0.01 M CaCl₂ electrolyte solution with 10 g/L solid concentrations.

After determining the sorption constants, the site density and the surface area of the amorphous aluminum oxide were investigated. To develop a uniform modeling approach across a wide range minerals, some researchers suggested a single constant total site density (2.31 sites/nm²) for all oxide solids. This could facilitate comparison of derived log K values (Davis and Kent, 1990; Payne et al., 2013; Turner and Sassman, 1996; Mathur and Dzombak, 2006). Turner and Sassman (1996) mentioned that this approach may not represent the exact processes operating at the interface, but it serves to establish baselines for future comparison

of modeling results by limiting the number of adjustable parameters. In this study, the site density is taken as 2.31 sites/nm² for all minerals. The surface area of the amorphous aluminum oxide is taken as 209 m²/g, as measured by Goldberg and Johnston (2001).

After adjusting the protonation/deprotonation constants and iodine sorption constants for amorphous aluminum oxide mineral by using Whitehead's (1974) I⁻ adsorption data, the obtained values of the constants are given in Eqs. (7)–(10).

These surface complexation reactions are used in geochemical simulation representing iodine-groundwater-rock interactions to obtain depth dependent K_d values.

3. Evolution of groundwater chemistry with depth

We have modeled the groundwater composition at different depths by referring to the study by Iwatsuki et al. (2005) at the Tono site in Japan, where sedimentary rock overlies granitic rock. This study has been utilized in the present study, because it shows detailed deep borehole data down to depths of 1000 m below ground level, including groundwater composition, temperature, pH and Eh measurements. With the data reported in this reference, we have modeled the evolution of groundwater compositions for the rock matrix and for the fracture filling materials (FFM). Results of these models have been compared with actual measured depth-dependent groundwater composition. Radionuclide sorption by the rock matrix and the FFM are considered separately in the transport model due to different mineral composition of the FFM and the rock matrix.

Conceptual groundwater-chemistry evolution with depth has been modeled by using the PHREEQC code with the LLNL database. In the model, it is assumed that the velocity of the water is slow so that equilibrium is reached between minerals and the constituents of the groundwater except for halite. As mentioned in JNC Report (2000,4), the model is limited in that it does not allow simulation of the concentration of chloride. Halite is used to add Cl⁻ ion into the system to complete the composition of groundwater for charge neutrality and completeness of the system. Saturation indexes of the halite are obtained from existing depth dependent groundwater data from Iwatsuki et al. (2005) by using PHREEQC.

It is assumed that sedimentary rock exists above granite. The rainwater is assumed as the recharge water in groundwater evolution and water is equilibrated with O₂ and CO₂ gases found in the atmosphere, resulting pH = 5.66, log PCO₂ = -3.5, log PO₂ = -0.7 (JNC, 2000,4). Equilibrated water is in contact with soil where the decay of organic substance and respiration of plant roots generate CO₂ gas. Partial pressure of CO₂ gas in the soil becomes 10–100 times more than in the atmosphere. In this study, it is assumed that the log P_{CO_2} = -1 (JNC, 2000,4; Stumm and Morgan, 1996). The CO₂-rich groundwater is in contact with sedimentary rock and then with granitic rock. In the groundwater evolution model at different depths, reactions related with mineral dissolution and precipitation, redox, and surface complexation are taken into account, but ion exchange reactions are not considered.

The Toki lignite bearing sedimentary rocks is composed of quartz (0.1%), plagioclase (21.5%), biotite (0.3%), amphibole (0.6%), calcite (0.1%), zeolite (0.4%), clay minerals (76.8%) and opaque minerals (0.8%) including pyrite (Sasamoto et al., 2004). To

Table 2

Data for calculating smectite and aluminum oxide in sedimentary rock, granitic rock matrix and FFM.

<i>Sedimentary rock</i>			
Dry density of sedimentary rock	1890 kg/m ³		
Porosity	30%		
Sedimentary rock contact with water	1890 g/L		
Bentonite content of sedimentary rock	76.8%		
Smectite content of bentonite	48%		
Aluminum oxide content	12%		
Availability	25%	50%	75%
Smectite amount	174.18 g/L	348.36 g/L	522.55 g/L
Aluminum oxide amount	56.7 g/L	113.4 g/L	170.1 g/L
<i>Granitic rock</i>			
Dry density of granitic rock	2650 kg/m ³		
Porosity	2%		
Granite contact with water	2650 g/L		
Aluminum oxide content	12% of granite		
Availability	25%	50%	75%
Aluminum oxide amount	79.38 g/L	158.76 g/L	238.14 g/L
<i>Fracture Filling Materials (FFM)</i>			
Dry density of FFM	2609 kg/m ³		
FFM amount	10% of fracture volume		
Groundwater	90% of fracture volume		
FFM contact with water	2609 * 0.1/0.9 = 290 g/L		
Aluminum oxide content	15% of FFM		
Aluminum oxide amount	43 g/L		

explain the mineral dissolution and precipitation reactions, albite, chalcedony, calcite, pyrite, hematite, sodium montmorillonite and halite minerals are used for the sedimentary rock and albite, quartz, calcite, K-feldspar, pyrite, annite, kaolinite and halite are used for granite. Iron minerals are used to determine the Eh, and sulfate content of the groundwater is determined by the solubility equilibrium of pyrite. Drake et al. (2006) showed from the mineralogy and geochemistry of the FFM at Forsmark and Oskarshamn in Sweden that abundant minerals in fractures are calcite, hematite, chlorite, clay minerals, quartz and alteration minerals of host rock. For the groundwater evolution in FFM, albite, quartz, calcite, pyrite, annite, kaolinite, hematite, and halite are assumed. Surface complexation reactions of bentonite and aluminum oxide are taken into account for the sedimentary rock and surface complexation reactions of aluminum oxide are considered for granitic rocks. Temperature change has also been taken into account by adopting measured temperature values at certain depths given in Iwatsuki et al. (2005).

The porosity may exceed 30–40% in sedimentary rocks such as the Neogene rocks that often overlie crystalline basement in Japan (JNC, 2000,4); the porosity of the sedimentary rock is assumed as 30% in this paper. In this study, bentonite is taken as the clay mineral. Related experiments on reactions between bentonite and water show that the equilibrium between bentonite and water depends on ion exchange reactions of smectite, dissolution equilibria of associated minerals, oxidation reactions and surface complexation reactions (Sasaki et al., 1995; Oda and Shibata, 1999; JNC, 2000,4). In Oda and Shibata (1999), the pH of the equilibrium water changed from alkaline to neutral as the bentonite to water ratio increased under anaerobic conditions. In the JNC report (2000,4), it is explained that this pH change resulted not only from ion exchange and mineral dissolution reactions but also from acid base reactions (protonation/deprotonation) of the edge sites of smectite and the dissolution of soluble impurities in bentonite. For modeling depth dependent groundwater evolution, a generalized two layer model is used to determine the effect of protonation/deprotonation reactions in the bentonite-water system on pH. This model was developed by Dzombak and Morel (1990), in which the protonation/deprotonation reactions and related equilibrium constants for smectite mineral were given as:

Specific surface area of the smectite is taken as 29 m²/g (JNC, 2000,4).

The aluminum oxide content of the Toki Lignite Bearing sedimentary rock ranges between 10.3% and 20.2% at the Mizunami Underground Research Laboratory site (Abdelgawad et al., 2009). In this study, aluminum oxide content of the sedimentary rock is assumed 12%. In order to use surface complexation reactions in the groundwater evolution model, the amount of the minerals that contact with water should be known.

For the groundwater chemistry evolution in granite located below the sedimentary rock as a function of depth, surface complexations of the aluminum oxide minerals for the rock matrix and the FFM are modeled. The specific surface area and site density have been assumed as 209 m²/g and 2.31 sites/nm² respectively for all minerals. To calculate the amount of aluminum oxide in the granite and the FFM, the chemical composition should be known. The chemical compositions of crystalline rock and FFM observed in Forsmark and Oskarshamn areas in Sweden have been used. In Forsmark area, the chemical composition of granite is 74.38% SiO₂, 12.92% Al₂O₃, 2.67% Fe₂O₃, 3.55% Na₂O, 1.57% CaO (Drake et al., 2006). In this study, the aluminum oxide content of the granite is assumed to be 12% for the rock matrix.

In order to calculate surface complexation reactions between minerals and groundwater in the granitic rock, it is assumed that the amount of mineral interacting with water is proportional with the rock porosity of 2% as given in JNC (2000,4). Besides this, all the minerals may not contact the water in the porous region; some of them may be buried within the rock while others may not contact with the water. In order to calculate the surface complexation reactions between minerals and groundwater in the rock matrix, it is assumed that the amount of minerals available for interactions with the water is proportional with the porosity of the rock matrix. We have made a parametric study to observe this effect by assuming 25%, 50% and 75% of the minerals in the rock matrix are in contact with water. The data is used to find available smectite and aluminum oxide amounts in order to calculate the solid

Fig. 1. Iodine speciation at initial iodine molalities 10^{-4} g atom/kg as a function of pH at 25 °C (a) Palmer et al. (1985), (b) with PHREEQC.

concentration for surface complexation reactions in the sedimentary rock is given in Table 2.

To determine the groundwater composition in the fractures, the composition of the FFM should be known. When the geochemistry and mineralogy of the FFM at Forsmark and Oskarshamn were investigated, it was seen that the aluminum oxide content of the FFM varied between 15% and 21.5% at KFM01A borehole at different depths in the Forsmark area (Drake et al., 2006). In this study, for conservativeness, the aluminum oxide content is taken as 15% and it is assumed that 10% of the fractures are coated with the FFM. The averaged measured dry density of altered zone at Kamaiishi mine in Japan is 2609 kg/m^3 (JNC, 2000,4). The dry density of the FFM is taken as 2609 kg/m^3 . Data for calculating the aluminum oxide amount in the FFM is given in Table 2.

After determining the mineral contents available for surface complexation reactions, the depth dependent groundwater evolution verification has been modeled with PHREEQC for the rock matrix and the FFM with the LLNL database for 25%, 50% and 75% availability of bentonite and aluminum oxide minerals that are in contact with water, and compared with the measured groundwater constituents around the Mizunami underground research laboratory in Japan (Iwatsuki et al., 2005).

It is observed that the groundwater evolution model using the assumption that 25% of the minerals are in contact with water in porous media is in good agreement with the measured values obtained from the site. Groundwater in and around the Mizunami Underground Research Laboratory construction site is classified into a Na–Ca– HCO_3 type in the upper sedimentary rocks and a Na–(Ca)–Cl type in the lower sedimentary rocks and the granite (Iwatsuki et al., 2005). The groundwater constituents for the rock matrix and the FFM obtained by PHREEQC modeling have been observed to be in good agreement with the measured values given in Iwatsuki et al. (2005).

4. Confidence to geochemical simulation

In the present study, geochemical simulations for radionuclide-groundwater–host rock interaction have been carried out to determine K_d values for various depths. As Oreskes et al. (1994) and Grambow and Bretesche, 2014; mention, validation of the modeling of natural systems is impossible, but it can be confirmed partially by comparing prediction with observation, which would provide confidence in the assessment.

Grambow and Bretesche, 2014; mentioned that the K_d model may become incorrect if mineral or water composition changes, while a surface complexation model may be able to capture such differences. In this study, the K_d value is obtained from depth dependent geochemical simulation of iodine-groundwater–rock interaction by using surface complexation reactions. To decrease the uncertainty in obtaining K_d values and to build a confidence in geochemical modeling usage, at certain steps, conformity of

the geochemical model with the actual conditions (or real environmental circumstances) is investigated by comparing PHREEQC simulation results with experimental or in situ measurement studies. For example, the results of an iodine speciation model can be compared with the Palmer et al. (1985) study, where they used experimental results to determine temperature dependent equilibrium constants for some iodine species and create a speciation model. As seen in Fig. 1, we could obtain predicted iodine species in good agreement with Palmer et al. (1985) study.

Surface complexation modeling is usually used to model adsorption on hydrous oxide minerals (Wang et al., 2001; Davis and Kent, 1990; Dzombak and Morel, 1990). For sorption modeling, surface acidity constants are required and they can be obtained from potentiometric titration data (Wang et al., 2001). In case of limited or no sorption data, LFERs can be used to determine these constants for cations or anions (Dzombak and Morel, 1990). Sorption modeling also involves adjusting the binding constants for surface reactions to minimize the differences between experimental and calculated values of the sorbed amount of radionuclide at each pH, under defined physical and chemical conditions (Wang et al., 2001). Due to limited data related with iodine sorption onto aluminum oxide mineral, LFERs are used in this study and adjustments are done based on the experimental data obtained by Whitehead (1974). Modeled iodine sorption onto amorphous aluminum oxide is given in Fig. 2 and the model represents the adsorption data very well. Surface complexation constants determined from this study will be reassessed when the acidity constants are obtained by using new potentiometric titration data.

Oreskes et al. (1994) explain that verification and validation of numerical models of natural systems is impossible due to the fact that natural systems are never closed and because model results are always nonunique. At the same time, they pointed out that impartial confirmation is possible by the demonstration of agreement between observation and prediction. Depth dependent groundwater evolution obtained from PHREEQC code in this study could be compared with in-situ observation at Tono Mine Site in Japan. The groundwater evolution model using the assumption that 25% of the aluminum oxide minerals are in contact with water in porous media is in good agreement with the measured values obtained from the site as given in Fig. 3.

5. Iodine transport model with depth-dependent transport parameters

In this study, the TTBX model developed by van den Akker and Ahn (2014) for the release and transport of radionuclides through multi-segmented geological media has been used for simulating iodine transport. See Fig. 4 for the model configuration of TTBX. The governing equations for the aqueous transport of the n -th member in an arbitrary length decay chain through the p -th seg-

Fig. 2. Iodine sorption onto amorphous aluminum oxide (Modified from Nagata et al., 2009).

ment in heterogeneous geological media are given in van den Akker and Ahn (2014).

For the present study, because the primary interest is transport of iodine-129, which has no precursors, the equations can be simplified for a single-radionuclide case, shown below for the reader's convenience:

$$R_p \frac{\partial C_p(x, t)}{\partial t} + V_p \frac{\partial C_p(x, t)}{\partial x} + \lambda R_p C_p(x, t) - \frac{D_p}{b_p} \frac{\partial W_p(x, z_p, t)}{\partial z_p} \bigg|_{z_p=0} = 0, \quad (13)$$

$$x_p > x > x_{p-1}, t > 0, p = 1, 2, 3, \dots,$$

and

$$\alpha_p \frac{\partial W_p(x, z_p, t)}{\partial t} - D_p \frac{\partial^2 W_p(x, z_p, t)}{\partial z_p^2} + \lambda \alpha_p W_p(x, z_p, t) = 0, \quad (14)$$

$$z_p > 0, x_p > x > x_{p-1}, t > 0, p = 1, 2, 3, \dots,$$

Where

$$R_p = 1 + \frac{\rho_p(1 - \phi_p)}{\phi_p} K_p, p = 1, 2, 3, \dots, \text{ and} \quad (15)$$

$$\alpha_p = \epsilon_p + \rho_p' K_p', p = 1, 2, 3, \dots \quad (16)$$

Eq. (13) is applied for advective transport in the p -th segment of the principal transport pathway ranging between x_{p-1} and x_p . The quantity $C_p(x, t)$ is the concentration of iodine-129 in the water phase in the pores in the segment. The segment has an aperture of $2b_p$ (m). The second term on the left side represents advection with the pore velocity of v_p (m/year). The third term expresses loss by radioactive decay with the decay constant λ (1/year) of iodine-129. The last term represents the molecular diffusion flux leaving the planar segment of planar water conduit into the surrounding porous rock matrix with the diffusion coefficient D_p . The sorption retardation coefficient R_p is defined as Eq. (15), in which the porosity ϕ_p and the density ρ_p of the porous material that fills the segment p are used. The coefficient K_p is the sorption distribution coefficient of iodine specie in segment p between the water and sorbed phases.

Eq. (14) is applied for the molecular diffusion process in the rock matrix surrounding the planar segment p , perpendicular to the planar segment. The quantity $W_p(x, z_p, t)$ is the concentration of iodine-129 in the water phase in the pores in the rock matrix. The capacity factor α_p , defined in Eq. (16), represents the sorption retardation. The porosity ϵ_p and the density ρ_p' of the rock matrix are also used in the formula. The sorption distribution coefficient K_p' of iodine between the water and sorbed phases in the rock matrix is also included in Eq. (16), and is different from K_p for the segment filling material.

If we assume that iodine 129 is released from a failed canister in the repository for a time period of T_L (years) congruently with the dissolution of waste form then the concentration of iodine at the fracture genesis is formulated as

$$C_1(0, t) = \frac{1}{v_1 \phi_1 A_1} \frac{M_0}{T_L} e^{-\lambda t} \{h(t) - h(t - T_L)\}, t > 0, \quad (17)$$

where the function h is a Heaviside step function, and M_0 is the initial inventory of iodine 129 in the waste canister, and A_1 is the cross sectional area of the segment connected with the failed waste canister. This can be determined by multiplying the fracture aperture ($2b_1$) by the total chord length of fractures intersecting the repository footprint allocated for a single canister. A value for the subsequent transport segments is adjusted to preserve volumetric flow.

The governing Eqs. (13) and (14) can be solved analytically with appropriate side conditions, as shown in van den Akker and Ahn (2014). The analytical solution is shown below for the reader's convenience:

Fig. 3. Depth dependent groundwater chemistry at 25% (▲) availability of bentonite and aluminum oxide minerals that contact with water (◇ represent the measured values in the area).

Fig. 4. Multi-segment model for one-dimensional advective transport with matrix diffusion (van den Akker and Ahn, 2014). For nomenclature of parameters, refer to the main text in Section 4.

$$C_p(x, t) = \frac{M_0}{T_L} \frac{\exp(-\lambda t)}{v_p \phi_p A_p} B_p(x, t), \quad t \geq 0, x_p \geq x \geq x_{p-1},$$

$$p = 1, 2, 3, \dots, \quad (18)$$

where

$$B_p(x, t) = h(t - t_R) \operatorname{erfc} \left(\frac{\left(\sum_{j=1}^{p-1} \frac{\sqrt{D_j z_j}}{b_j v_j} (x_j - x_{j-1}) \right) + \frac{\sqrt{D_p z_p}}{b_p v_p} (x - x_{p-1})}{2(t - t_R)^{\frac{1}{2}}} \right)$$

$$- h(t - t_R - T) \operatorname{erfc} \left(\frac{\left(\sum_{j=1}^{p-1} \frac{\sqrt{D_j z_j}}{b_j v_j} (x_j - x_{j-1}) \right) + \frac{\sqrt{D_p z_p}}{b_p v_p} (x - x_{p-1})}{2(t - t_R - T)^{\frac{1}{2}}} \right),$$

$$p = 1, 2, 3, \dots, \quad (19)$$

$$\text{and } t_R = \sum_{j=1}^{p-1} \left(\frac{R_j}{v_j} (x_j - x_{j-1}) \right) + \frac{R_p}{v_p} (x - x_{p-1}), \quad p = 1, 2, 3, \dots \quad (20)$$

Note that t_R represents the retarded travel time from the source ($x = 0$) to the observation point.

We first discretize the pathway of iodine in the geological formations into a few segments, within each of which the values of the parameters are assumed to be constant but are evaluated by the formulas shown in Section 5. For the sorption distribution coefficients, K_p and K'_p , for the filling materials in the advection channel and for the rock matrix, respectively, we perform geochemical simulation using PHREEQC, as discussed in Sections 2 and 3. In Sections 6 and 7, we will observe transport of iodine-129 by taking into account the depth-dependency of the parameters.

6. Depth-dependent parameters

Depth-dependent parameters can be categorized into three groups. The first group is the basic physical parameters, including temperature, pressure, density and viscosity of water. The second group is the transport parameters, including the pore velocity of water, and the diffusion coefficient of iodine. The third group is

the geochemical parameters, including pH, Eh, iodine speciation in groundwater and sorbed phases, and the retardation coefficient of iodine.

Groundwater velocity in a planar fracture is formulated by the cubic law (Snow, 1965):

$$v = \frac{\rho g}{\eta} \frac{1}{2(S+b)} \frac{(2b)^3}{12} i, \quad (21)$$

where ρ is water density (kg/m^3), g the gravitational acceleration (m/s^2), η the viscosity of water (Pa s), $2S$ the spacing between two adjacent fractures (m) (taken as 1 m arbitrarily), $2b$ the fracture aperture, and i the hydraulic gradient (m/m), which has been set as 0.1 in the present calculations arbitrarily. In this study, groundwater evolution modeling is based on the groundwater composition at Tono site in Japan. To be consistent with it, we used the value observed there. In the JNC report (2000, 1), it is mentioned that although few data exists to define deep hydraulic gradients for a generic host rock in Japan, they use database of groundwater table slopes. In that study, the frequency of hydraulic gradient distribution at the Kamaishi Research site fitted to log normal distribution between 10^{-3} and 0.1. In our study, the hydraulic gradient is taken as 0.1. In this formula, we need to determine the values of these parameters as functions of depth, which are discussed and summarized below.

According to Wei et al. (1995), the fracture aperture is given as

$$\frac{b}{b_0} = 1 - \frac{Z}{58 + 1.02z}, \quad (22)$$

where b_0 is the half fracture aperture at the ground surface, and b is the half fracture aperture at depth Z (m).

The water density ρ is formulated as (Kell, 1975):

$$\rho = \rho_a (1 + (P - P_a) K_T) \quad (23)$$

where ρ_a is the density of water depending on temperature $T(^{\circ}\text{C})$ at the atmospheric pressure P_a . The formula for ρ_a in the range of 0–150 $^{\circ}\text{C}$ is given as

$$\rho_a = \frac{999.83952 + 16.945176T - 7.9870401 \times 10^{-3}T^2 - 46.170461 \times 10^{-6}T^3 + 105.56302 \times 10^{-9}T^4 - 280.54253 \times 10^{-12}T^5}{1 + 16.879850 \times 10^{-3}T}. \quad (24)$$

The isothermal compressibility κ_T [bar^{-1}] is calculated from the following formula in the range from 0 to 100 °C as

$$10^6 \kappa_T / \text{bar}^{-1} = (50.88496 + 0.6163813T + 1.459187 \times 10^{-3}T^2 + 20.08438 \times 10^{-6}T^3 - 58.47727 \times 10^{-9}T^4 + 410.4110 \times 10^{-12}T^5) / (1 + 19.67348 \times 10^{-3}T), \quad (25)$$

The viscosity η of water is also dependent on temperature (T) and pressure (P) (Harris and Woolf, 2004):

$$\eta = \exp \left(a_1 + a_2P + \frac{a_3P}{T} + a_4P^2 + \frac{a_5P^2}{T} + a_6P^3 + \frac{a_7}{T} + \frac{a_8}{T^2} \right), \quad (26)$$

where coefficient values are $a_1 = 0.411011$, $a_2 \times 102/\text{MPa}^{-1} = 0.854113$, $a_3 \times 10^{-1}/(\text{K MPa}^{-1}) = -0.267340$, $a_4 \times 104/\text{MPa}^{-2} = -0.135750$, $a_5 \times 102/(\text{K MPa}^{-2}) = 0.525404$, $a_6 \times 108/\text{MPa}^{-3} = -0.515042$, $a_7 \times 10^{-4}/\text{K} = -0.235032$, $a_8 \times 10^{-6}/\text{K}^2 = 0.654401$.

Temperature T (°C) and pressure P (Pa) change with depth Z (m) as:

$$T = 15 + 0.03Z, \text{ and} \quad (27)$$

$$P = \rho_M gZ \quad (28)$$

where ρ_M is the density of overlaying materials (kg/m^3).

The diffusion coefficient D_0 of a spherical particle in an unconfined liquid is formulated in terms of temperature (K), the dynamic viscosity η of the liquid and the hydrodynamic radius of the particle a (m) determined by the Stokes–Einstein equation (Alonso et al., 2007) as

$$D_0 = \frac{kT}{6\pi\eta a} \quad (29)$$

where k is the Boltzmann constant. The diffusion coefficient in the host rock is defined by multiplying D_0 with the porosity of the rock matrix and the tortuosity correction factor, which is taken as 0.055 (Ahn, 1998).

Depth dependency of the capacity factor α_p of the host rock defined by Eq. (16) and the retardation factor R_p of the fracture filling material defined by Eq. (15) has been taken into consideration by applying the depth dependency of the sorption distribution coefficients included in the respective formulations. The porosity $\phi_p = 0.9$ and the density $\rho_p = 2.609 \text{ kg/m}^3$ of the porous material that fills the segment p are assumed the same for all the segments. Similarly, the porosity $\varepsilon_p = 0.02$ and the density $\rho'_p = 2.650 \text{ kg/m}^3$ of the rock matrix are assumed the same for all the segments. With the models for iodine speciation, iodine sorption and groundwater evolution as discussed in Sections 2 and 3, the depth-dependent iodine-groundwater-rock interactions are modeled to obtain depth-dependent K_d values for the rock matrix and the FFM. In the modeling, depth dependent temperature and pressure variation have been also taken into account.

7. Cases for numerical simulations

In this section, iodine migration in granitic rock is modeled for hypothetical repositories at two different depths (500 and 1000 m) as shown in Figs. 5a and 6a. Granite is assumed to extend under sedimentary rock, which is 100 m thick below the surface. The granite between 100 and 1,000 m depth is divided into four regions.

In the first case, the repository is located at 500 m depth. The granitic rock extends for 400 m (between the 100 and 500 m depths) (Fig. 5a) and is divided into two layers with 200 m in thickness each. At the repository horizon at the 500-m depth, the

horizontal path of 100-m length connecting the point of radionuclide release with the major fracture running vertically is assumed. Thus, the transport pathway consists of three segments as shown in Fig. 5b. The depth-dependent parameters in each segment are numerically evaluated by the formulas summarized in Section 5 at the mid-depth, respectively. For the first segment, the depth is 500 m, while for the second and third segments the depths are 400 and 200 m, respectively. Fig. 5b shows the length of each segment. The aperture becomes greater as close to the surface by formula (22). In this formula, the reference fracture aperture b_0 set at 300 m is assumed 1×10^{-4} m as given in Yoon and Ahn (2010).

In the second case, the repository is located at 1000 m depth. The granitic rock extends for 900 m (between the 100 and 1000 m depths) (Fig. 6a) and is divided into four layers. The bottom two layers have thickness of 250 m, while the top two layers have 200 m thickness. Similar to Case 1, there is a 100 m long horizontal path at the repository horizon that connects the point of release and the major fracture. The depth-dependent parameters have been evaluated at the mid-depth point of each segment, i.e., 1000, 875, 625, 400, and 200 m from the bottom. Fig. 6b shows the length of each segment. The reference fracture aperture at 300 m is assumed 1×10^{-4} m.

For each case, distribution coefficients for each segment have been calculated using the PHREEQC code for the main interactions among iodine, groundwater, and rock as mentioned in Sections 2 and 3. To calculate sorption retardation coefficient given in Eq. (15), the interaction among iodine, groundwater and the FFM has been simulated for each segment. PHREEQC simulations yielded concentrations at equilibrium of iodine in groundwater and in the sorbed phase onto the FFM. The results show that the groundwater is in reduced alkaline conditions, and iodine is found as I^- form, for which sorption distribution coefficients onto aluminum minerals in the geological formation have been found to be very low, but still dependent on depth. The distribution coefficients for the FFM have been calculated by taking the ratio of these equilibrium concentrations given in Table 3. Similarly, the capacity factor in Eq. (16) has been calculated by simulating interaction among iodine, groundwater and rock minerals at each segment. The results are tabulated in Table 3.

The values of input parameters for TTBX calculations set for cases 1 and 2 are summarized in Table 4.

8. Numerical results and discussions

The first comparison has been made between the two cases for the same source condition, in which the constant release of total 3.3853 mol of iodine 129 from a failed canister of spent nuclear fuel over 1 million years has been assumed (see Eq. (17)). This amount of iodine has been determined by assuming 1758 metric ton of spent fuel, as given in Yoon and Ahn (2010).

For both repository depths (Figs. 7 and 8), the concentration change as a function of time has been observed at the end of each three segment. Note that the locations of the exits of the three upper segments (at $x = 677$, 908 and 1139 m, respectively) for the 1000 m-deep repository (Case 2) correspond to the exits of three segments (at $x = 100$, 331 and 562 m) for the 500 m-deep repository (Case 1). Therefore, the results for these three locations can be compared with each other to see the effects of repository depth.

Radionuclide concentration evolution as a function of time shown in 8 indicates that most of the iodine concentration is retained within the first segment (at 100 m) and that the amount of iodine that reaches the end of the second segment (at 388.5 m) is considerably reduced. The decrease in concentration continues from the second segment trough end of the fourth

Fig. 5. Schematic view for (a) repository at 500 m and (b) fracture configuration throughout migration pathway in heterogeneous rock formation.

Fig. 6. Schematic view for (a) repository at 1000 m and (b) fracture configuration throughout migration pathway in heterogeneous rock formation.

Table 3

Geochemical simulation (PHREEQC) results of depth dependent iodine-groundwater-rock interaction for two cases.

Region	T (°C)	P (MPa)	Rock Matrix			Fracture Filling Mineral		
			Iodine in water (mol/L)	Sorbed iodine (mol/kg)	Kd (m³/kg)	Iodine in water (mol/L)	Sorbed iodine (mol/kg)	Kd (m³/kg)
Case 1								
100–300	21	4.45	9.99×10^{-6}	1.12×10^{-8}	1.12×10^{-6}	9.99×10^{-6}	8.34×10^{-9}	8.35×10^{-7}
300–500	27	9.65	9.96×10^{-6}	3.67×10^{-8}	3.68×10^{-6}	9.97×10^{-6}	2.81×10^{-8}	2.82×10^{-6}
500	30	12.25	9.95×10^{-6}	5.11×10^{-8}	5.14×10^{-6}	9.96×10^{-6}	4.17×10^{-8}	4.19×10^{-6}
Case 2								
100–300	21	4.45	9.99×10^{-6}	1.12×10^{-8}	1.12×10^{-6}	9.99×10^{-6}	8.34×10^{-9}	8.35×10^{-7}
300–500	27	9.65	9.96×10^{-6}	3.67×10^{-8}	3.68×10^{-6}	9.97×10^{-6}	2.81×10^{-8}	2.82×10^{-6}
500–750	33.8	15.50	9.93×10^{-6}	6.89×10^{-8}	6.93×10^{-6}	9.95×10^{-6}	5.4×10^{-8}	5.45×10^{-6}
750–1000	41.3	22.00	9.88×10^{-6}	1.18×10^{-7}	1.20×10^{-5}	9.90×10^{-6}	9.55×10^{-8}	9.64×10^{-6}
1000	45	25.25	9.85×10^{-6}	1.54×10^{-7}	1.57×10^{-5}	9.90×10^{-6}	9.88×10^{-8}	9.98×10^{-6}

Table 4

The input parameters for Case 1 and Case 2.

Segment		Water	Water	Fracture	Cross Sect.		R	Capacity	
		Density (kg/m ³)	Viscosity (Pa.s)	Aperture (m)	Area A	V (m/y)		Factor α	D _{eff} (m ² /y)
Case 1									
100–300	3	999.98	9.82×10^{-4}	1.35×10^{-4}	1.637×10^{-4}	6.40	1.002	0.02297	3.70×10^{-5}
300–500	2	1000.80	8.53×10^{-4}	8.06×10^{-5}	6.630×10^{-4}	1.58	1.008	0.02974	4.34×10^{-5}
500	1	1001.06	7.99×10^{-4}	6.81×10^{-5}	1.028×10^{-3}	1.02	1.012	0.03359	4.68×10^{-5}
Case 2									
100–300	5	999.98	9.82×10^{-4}	1.35×10^{-4}	2.973×10^{-5}	6.40	1.002	0.02297	3.70×10^{-5}
300–500	4	1000.80	8.53×10^{-4}	8.06×10^{-5}	1.204×10^{-4}	1.58	1.008	0.02974	4.34×10^{-5}
500–750	3	1001.27	7.40×10^{-4}	5.77×10^{-5}	2.847×10^{-4}	0.67	1.016	0.03835	5.12×10^{-5}
750–1000	2	1001.33	6.43×10^{-4}	4.52×10^{-5}	5.140×10^{-4}	0.37	1.028	0.05170	6.04×10^{-5}
1000	1	1001.21	6.03×10^{-4}	4.12×10^{-5}	6.379×10^{-4}	0.30	1.029	0.06151	6.51×10^{-5}

segment (at 908 m) with a declining rate. However, it is seen that the concentration at the exit of the last segment (at 1139 m) is almost same with the previous segment. This indicates that the iodine is not retained in the last segment due to an increasing groundwater velocity at a shallow depth.

For the repository at 500 m (Fig. 7), the difference in the iodine concentration between the second and the third segments is negligible; most of the iodine at the exit of segment 1 moves

through the fracture and reaches the exit of the last segment. However, for the repository at 1000 m (Fig. 8), iodine is effectively retained in the first two segments, resulting in much smaller concentration at the top of the granite layer. The blue dash line for 1139 m in Fig. 8 and the red line for 562 m in Fig. 7 show the concentration change at the same location, i.e., at the top of granite as shown in Fig. 5. From this comparison, it is observed that the repository depth has a significant effect on migration and retention

Fig. 7. Concentration change in the fracture as a function of time for ^{129}I migration from the repository at 500 m depth (Case 1).

Fig. 8. Concentration change in the fracture as a function of time for ^{129}I migration from the repository at 1000 m depth. The locations at $x = 677$, 908 and 1139 m, respectively, for the 1000 m-deep repository (Case 2) correspond to those at $x = 100$, 331 and 562 m for the 500 m-deep repository (Case 1, Fig. 7).

Fig. 9. Profiles of iodine-129 concentration along the water flow pathway from the repository located at the depth of 500 m. The dashed vertical lines indicate the interfaces between segments.

Fig. 10. Profiles of iodine-129 concentration along the water flow pathway from the repository located at the depth of 1000 m. The dashed vertical lines indicate the interfaces between segments.

of the radionuclide; locating a repository at a greater depth is effective in confining iodine 129 in the geological formation.

Very weak sorption is assumed throughout the pathway; the retardation factor is slightly greater than 1 in any segments. Yet, iodine is retained within the layers around a repository if it is located at a great depth. This can be explained by matrix diffusion into the rock matrix around the fracture. The fracture aperture decreases with increasing depth, and water flow velocity in the fracture becomes smaller significantly due to the cubic law. Effective diffusion coefficient increases with increasing temperature and decreasing viscosity. These changes make contribution of the matrix diffusion more significant in relation to advection through the fracture, so that more iodine can be retained in the vicinity of the repository if it is located at a greater depth.

Iodine concentration profiles in the fracture as a function of distance for two repository depths are shown in Figs. 9 and 10. Note that the release of iodine from the canister continues for the first million years. After that, uncontaminated water flows into the multi-segment pathway at $x = 0$. The profiles for 10 million years indicate the distribution of iodine after the source has been depleted.

In case of the 500-m repository (Case 1, left Fig. 9), iodine has reached the exit of the third segment, i.e., the interface between the granite and sedimentary rock within 1 million years. After that, iodine is released to the biosphere through the aquifers in the sedimentary layer. In the case of the 1000-m repository, iodine stays within the first segment, and has never gone beyond it.

In each profile, it is observed that the front of the iodine plume is substantially retarded, compared with the advection front. For example, for segment 1 in Case 1, the water velocity in the fracture is assigned to be 1.02 m/year (Table 4). The length of the segment is 100 m. Thus, the advection front passes the exit of segment 1 a little before 100 years. However, the profile for 100 years in Fig. 9 stays within 30 m range. This retardation effect becomes more prominent in Case 2 (right Fig. 10) because the water velocity in segment 1 is substantially smaller due to the greater depth and because the molecular diffusion coefficient into the rock matrix is greater.

After 1 million years, the iodine in the rock matrix in the vicinity of the source diffuses back to the fracture, and is further transported by advection along the fracture, but at the front of the plume along the fracture, iodine again diffuses into the rock matrix. Thus, iodine is retained in the vicinity of the source point for a long time.

9. Conclusions

In this study, migration of iodine 129 has been simulated to understand the effects of the depth of a repository by implementing depth dependency of various parameters, such as temperature and pressure, which in turn affect the transport properties such as water velocity and diffusion coefficient, and geochemical reactions of iodine with minerals and water. Detailed geochemical simulation has been conducted using the PHREEQC code to obtain the sorption distribution coefficients of iodine at various depths. The geochemical simulation has been benchmarked with experimental results and other simulation published earlier. Transport of iodine has been simulated by the one-dimensional, multi-segment transport code TTBX. Depth dependency of the parameters has been implemented in the TTBX simulation by assigning parameter values for each segment. Numerical results for iodine concentrations for two different repository depths have been obtained and compared.

Sorption of iodine has been observed very weak throughout the pathway; the retardation factor is only slightly greater than 1 everywhere. However, iodine is retained within the layers around a repository if the repository is located at a depth of 1000 m. This

can be explained by strong matrix diffusion in relation with the decreasing groundwater velocity at greater depth. The dominant retention mechanism at these levels is matrix diffusion due to a smaller fracture aperture and slower groundwater flow. Most of the iodine will stay within the deep layers near the repository, if it is located at 1000 m depth. Thus, it has been found that depth of the repository has significant effect on the retention of iodine.

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