# Electromigration experiments for studying transport parameters and sorption of cesium and strontium on intact crystalline rock

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A B S T R A C T

This study aims to determine upscaling factors for the radionuclides' distribution coefficients ($K_d$) on crushed rocks to intact rock for the safety analysis of radionuclide migration from spent nuclear fuel in bedrock towards biosphere. Here we report the distribution coefficients for intact rock determined by electromigration sorption experiments and compare the results with those from recently performed batch sorption experiments. In total 34 rock samples, representing three typical rock types from Olkiluoto Finland, were studied in order to determine distribution coefficients, effective diffusion coefficients and porosities using the electromigration sorption experiments, formation factor experiments and porosity measurement. The parameters determined represent the three main parameters of geosphere used in the safety assessment of spent nuclear fuel disposal. The distribution coefficients of cesium and strontium on intact rock varied between $(0.12\text{–}26.2) \times 10^{-3}\,\mathrm{m^3/kg}$ and $(1.4\text{–}13.3) \times 10^{-3}\,\mathrm{m^3/kg}$, respectively, whereas recent results for crushed rock varied between $(2\text{–}57) \times 10^{-3}\,\mathrm{m^3/kg}$ and $(17\text{–}40) \times 10^{-3}\,\mathrm{m^3/kg}$, respectively. This implies that crushing increases the distribution coefficient significantly and upscaling factors from 3 to 33 were determined for scaling the distribution coefficients of crushed rock to ones of intact rock. The determined distribution coefficients of cesium and strontium for intact rock can be directly applied in the safety assessment whereas the upscaling factors can be used to convert distribution coefficients determined for crushed rock into ones for intact rock. Based on the results for porosities and effective diffusion coefficients it was concluded that they do not seem to correlate with sorption parameters. However, an alteration state, heterogeneity and mineral content seem to be important factors affecting the distribution coefficients and upscaling factors.

## 1. Introduction

In Finland, the spent nuclear fuel from the currently operating nuclear power reactors will be disposed of in a bedrock repository at a depth of about 400 m. In the final disposal of spent nuclear fuel in geological formations, such as bedrock in Finland, the rock above the waste acts as the last barrier against the release of radionuclides into the biosphere. This has been taken into account in the safety assessment of the final disposal concept by the evaluation of the transport properties of radionuclides in the bedrock. The retardation mechanisms of radionuclides in bedrock are matrix diffusion and sorption on the minerals (Posiva, 2013). In the safety assessment effective porosity, diffusion coefficient and distribution coefficient ($K_d$) define the transport properties of the rock, and the magnitude of matrix diffusion and sorption. The effective diffusion coefficient depends only slightly on the considered radionuclide while the distribution coefficient varies

strongly from radionuclide to another. Furthermore, the transport parameters, especially the distribution coefficient, depend on the rock type and the mineral composition of rock. The porosity is fairly straightforward to determine while the distribution and effective diffusion coefficient offer challenges, particularly in case of crystalline rock. The distribution coefficients are typically determined using crushed rock. This, however, creates new surface area (directly in contact with water molecules) capable of sorbing radionuclides and thus distribution coefficients determined using crushed rock samples overestimate the distribution coefficient of intact rock. It has been found out that the distribution coefficients determined using crushed rock can be significantly higher than the ones determined using intact rock (Crawford, 2010). Furthermore, the batch sorption experiments are typically performed using a water-rock ratios that are not realistic for intact rocks. The diffusion coefficients, on the other hand, are typically measured using long-lasting and tedious experiments.

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**Table 1**

The average mineral contents (volume-%) of the Olkiluoto rocks used in the electromigration sorption experiments determined by the thin section method (all samples), by MLA and XRD (PP309 and PP219), and by FESEM-EDS (KR56 and PP175). Thin section results are averaged over three independent measurements and MLA results over two. For KR43, PP131(51), PP131(70) and PP249 the mineral contents were taken from Kärki and Paulamäki (2006). PP131(51) and PP131(70) are taken from the same drill core but from different locations (indicated in parentheses). The most effective sorbing minerals are highlighted.

| | TGG | | | MGN | | | PGR |
|---|---|---|---|---|---|---|---|
| | KR56 | PP175 | KR43 | PP309 | PP219 | PP131(51) | PP131(70) and PP249 |
| Sampling depth (m) | 815 m | 103 m | 40 m | > 284 m* | > 285 m* | 229 m | 248 m, 430 m |
| Number of sub samples (Cs) | 2 | 3 | 5 | 6 | 4 | 3 | 2 + 3 |
| Number of sub samples (Sr) | | 4 | | | 2 | | |
| Plagioclase | 36.8 ± 3.5 | 33.8 ± 0.8 | 34 ± 8 | 37.9 ± 7.1 | 27.5 ± 6.6 | 17 ± 7 | 17 ± 9 |
| K-feldspar | 25.5 ± 3.6 | 4.7 ± 4.6 | 12 ± 11 | 5.9 ± 4.1 | 5.3 ± 4.7 | 6.4 ± 3.7 | 33 ± 18 |
| Quartz | 33.8 ± 2.4 | 19.8 ± 2.1 | 24 ± 6 | 25.8 ± 3.4 | 27.2 ± 4.0 | 31 ± 10 | 35 ± 14 |
| **Biotite** | 3.3 ± 2.2 | 27.5 ± 2.6 | 23 ± 7 | 12.0 ± 6.3 | 29.0 ± 6.4 | 21 ± 8 | 0.9 ± 1.7 |
| **Muscovite** | 0.7 | 0.8 ± 0.7 | 0.3 ± 0.5 | 0.3 ± 0.3 | 1.4 ± 1.2 | 0.7 ± 0.7 | 2.5 ± 2.8 |
| **Sericite** | | | 0.3 ± 0.6 | 1.3 | 1.7 | 0.3 ± 0.4 | 1.2 ± 2.9 |
| **Pinite** | | | 0.1 ± 0.2 | | ~1 | 9.2 ± 7.6 | 0.4 ± 1.7 |
| Chlorite | 0.1 | 1.1 ± 0.8 | 0.3 ± 0.5 | 15.6 ± 13.5 | 2.9 ± 3.6 | 3.8 ± 5.2 | 0.7 ± 0.9 |
| Pyroxene | | 7.3 ± 0.7 | | | | | |
| Apatite | | 4.2 ± 1.0 | 1 ± 1 | | | 0.2 ± 0.2 | |

*Starting location of drilling with dips of $-89.9^{\circ}$ (PP309) and $-89.5^{\circ}$ (PP219).

There are a great number of distribution coefficients determined by batch sorption experiments available (Hakanen et al., 2012). Currently conservative estimates for the upscaling factors have to be used before they can be used to estimate the distribution coefficient of intact rock in the safety assessment. However, their utilization using less conservative approaches would be beneficial and it has not been thoroughly investigated so far. To this end, a systematic study to determine the upscaling factors for distribution coefficients from crushed to intact rock was performed. The distribution coefficient of cesium and strontium were determined for the most common rock types of Olkiluoto using the electromigration sorption experiments on drill core samples. In order to obtain the factors suitable for upscaling, these results were compared with the ones determined using batch sorption experiments in a recent study (Lehto et al., 2018). Cesium and strontium exist as cations in aqueous solutions ($Cs^+$ and $Sr^{2+}$) and their sorption mechanism on mineral surfaces is ion exchange that can be taken into account in safety assessment using $K_d$-concept. In crystalline rock samples, mica minerals have the highest sorption capacity of cesium and the ion exchange takes place on basal planes on crystal surfaces, frayed edge sites and third-type sites (Kyllönen et al., 2014).

The electromigration sorption experiments have been previously developed and tested by André et al. (2006, 2008, 2009). The method is based on enhancing the migration of ions into the intact rock by applying electrical potential over a drill core sample. Due to the enhancement, longer rock cores can be used than in traditional through diffusion experiments (Tachi et al., 2015) and thus effects arising from sample preparation, e.g. drilling and sawing, are reduced. Due to the experimental setup, the measurement cannot be used for determining effective diffusion coefficients. However, they were estimated using the same experimental setup by performing electrical resistivity measurements that offer information on a formation factor and can be used further to estimate the effective diffusion coefficient (Löfgren and Neretnieks, 2003). The method has been widely used in a Swedish program of the spent nuclear fuel disposal and its limitations and advantages have been thoroughly discussed by Löfgren (2015). In general, the method is faster than traditional through diffusion experiments that are used for determining the effective diffusion coefficient. The method has been further developed in order to perform the through electromigration experiments (Löfgren and Neretnieks, 2006). Furthermore, the porosities of the samples were determined using water saturation and immersion methods (Voutilainen et al., 2012).

This work aims to determine the three most important transport parameters of bedrock (distribution coefficients, effective diffusion coefficients and porosity) related to safety assessment for intact rock samples. The aim is to test the experimental methods for a wide range of rock samples from Olkiluoto, Finland, and to produce transport parameters that can be used directly in safety assessment. Furthermore, we propose the upscaling factors for converting the distribution coefficients obtained by batch sorption experiments with crushed rock into ones for intact rock. The rock samples and their mineral compositions as well as the electrical methods for measuring effective diffusion coefficient and distribution coefficient and porosity measurements are described in the work.

## 2. Materials and methods

### 2.1. Bedrock of Olkiluoto

Olkiluoto bedrock consists of four major rock types (contents given in parentheses): migmatitic gneisses (64%), pegmatitic granites (20%), gneisses (9%) and tonalite-granodiorite-granite gneisses (8%). The main minerals in these rocks are quartz (25–35%), potassium feldspar (5–35%), plagioclase (15–35%) and biotite (10–30%) (Kärki and Paulamäki, 2006). An exception for biotite is the pegmatitic granite, the biotite content of which is low (round 1%). In addition to biotite, these rocks contain other mica minerals (e.g. muscovite) but at lower content. The rocks contain also pinite and sericite, the alteration products of cordierite and plagioclase. These minerals are known to have a major effect to sorption capacity (due to their mineral structure, alteration state and chemical composition) of the rock and thus to the retention of radionuclide migration in crystalline rocks (Torstenfelt et al., 1982).

### 2.2. Rock samples

The electromigration sorption experiments were done with altogether 32 drill core samples (26 for cesium and 6 for strontium). Furthermore, formation factors and effective diffusion coefficients were measured for 24 and porosities for all 32 of these samples. The selected samples represent three of the typical rock types in Olkiluoto: mica gneiss (MGN), tonalite-granodiorite-granite gneiss (TGG), and pegmatitic granite (PGR). For four MGN and TGG drill core samples (PP309, PP219, KR56, PP175) the mineralogical composition was determined by several methods (see Table 1). For these samples batch experiments were done as a function of grain size and as a function of cesium and strontium concentration and the specific surface areas of various grain sizes were measured (Lehto et al., 2018). The samples for these experiments were taken from the same drill cores as close as possible to the drill core samples for the electromigration sorption experiments

**Fig. 1.** The sawed rock samples of drill cores PP219 and PP309. The samples 219A, 219D, 219H, 219 L, 309A, 309D, 309H and 309 L were used in the electromigration sorption experiments of cesium. The electromigration of strontium was studied with the samples 219B and 219E. The rock slices 219F, 219 J, 219 K, 309F, 309 J and 309 K were used in the determination of minerals by the thin section method. The rest was crushed and sieved for the batch sorption experiments and specific surface area measurements (Lehto et al., 2018).

(see Fig. 1). For four other drill cores (KR43, PP131(51), PP131(70), PP249) only one batch sorption experiment was done using the equilibrium concentrations of cesium and strontium from the electromigration experiments. The mineral contents of these latter four rock samples in Table 1 are the average values of the minerals in these rock types and they were taken from Kärki and Paulamäki (2006).

The drill core samples (diameter 50 mm) were cut with a diamond blade saw to 3–30 mm long sections for the electromigration sorption experiments. As an example, two MGN drill cores are shown Fig. 1. Exactly the same samples were used in porosity and electrical formation factor measurements.

### 2.3. Volumetric porosity experiments

The volumetric porosities of the drill core samples were determined by the water saturation method. First, the samples were dried in a vacuum to a constant weight. The bulk volumes of the rock samples were determined by a water immersion method (Voutilainen et al., 2012). Then the samples were put into a vessel where vacuum was pumped and deionized water (Millipore milli-Q) was added to the vessel. The rock samples were saturated under water for three weeks. Then the weights of the rock samples were measured after their surfaces were quickly dried. The difference of the dry and wet weights gave the amount of water inside the rock. The volume of the water and further the volumetric porosities of the rock samples were determined using the density of water and the bulk volumes of the samples. Possible systematical uncertainty sources of the experiment arise from remaining water after drying and remaining air after water saturation. Here the drying and water saturation were continued until constant weight in order to minimize the effect of these uncertainty sources.

### 2.4. Electromigration sorption experiments

The experimental setup for electromigration is presented in Fig. 2. The setup consists of an experimental vessel that was made of acrylic plastic and it contained two chambers that were separated by a drill core sample. The chambers were filled with 0.01 M NaCl solution and platinum electrodes were placed in the chambers. In order to prevent creation of pH and concentration gradients over the sample due to the electric current, solutions in the chambers were mixed continuously with each other using a peristaltic pump. The flow of solution from chamber to the other was made drop-wise to prevent the electrical connection along the water column in tubes. Before adding the cesium and strontium tracers an electrical potential over the sample was applied and it was kept for at least two weeks in order to stabilize the system. After this, $^{134}CsCl$ ($1 \times 10^{-4}$ M CsCl) or $^{85}SrCl_2$ ($1 \times 10^{-6}$ M SrCl$_2$) was added into the NaCl solution and the tracer concentration in the chambers was measured by taking samples of the mixed solution. The total volume of solution varied from 233 ml to 403 ml. The total

volume of solution was kept constant by adding deionized milli-Q water in order to compensate the decomposed water (to H$_2$ and O$_2$) due to electrolysis at the electrodes. The concentrations of cesium and strontium were determined by measuring their activity in the water samples using a gamma counter (Perkin Elmer 1480 Wizard). After the measurement, the water samples were brought back into the experimental system in order to maintain the total activity of the solution. The measured concentrations were then compared with the initial concentrations and the K$_d$ values of $^{134}$Cs and $^{85}$Sr for the rock samples were determined using equation:

$$K_d = \frac{V \times s\%}{m \times (100 - s\%)} \tag{1}$$

where V is the total volume of the solution, s% is the sorption percentage and m is the mass of the rock sample.

### 2.5. Formation factor and effective diffusion coefficient experiments

The formation factors of the drill core samples were determined using the electrical method (Löfgren and Neretnieks, 2003). Before the experiments, the drill core samples were saturated with 0.01 M NaCl solution for two weeks and the saturated samples were then placed in the electromigration system described in the previous section. The voltage over the rock sample was then gradually increased from 1 V to 30 V and the electric current through the rock sample was measured as a function of the voltage.

Following analysis was performed in order to determine the formation factors from measured data. First the resistivity of the rock sample ($\rho$) was determined by using equation (Löfgren and Neretnieks, 2003):

$$\rho = \frac{A}{l}\left(\frac{\Delta U}{I} - \frac{2l_w}{\kappa_w A_e}\right) \tag{2}$$

where A is cross sectional area of the rock sample and l is the length of the rock sample, $\Delta U$ is the measured electrical potential over the rock sample, I is the measured electric current, $l_w$ is the thickness of the water column between the sample and the electrode, $\kappa_w$ is the conductivity of the solution and A$_e$ is the inner surface area of the chamber. The formation factor (F$_f$) can then be determined from the resistivity of the rock sample by using equation (Löfgren and Neretnieks, 2003):

$$F_f = \frac{1}{\rho \kappa_w}. \tag{3}$$

In practice the F$_f$ is a measure for pore structures influence on the resistance of the sample. Typically, the effective diffusion coefficient (D$_e$) can be estimated from F$_f$ using the equation:

$$D_e = F_f D_0 \tag{4}$$

where D$_0$ is the diffusion coefficient of the tracer ion in water. Here it is
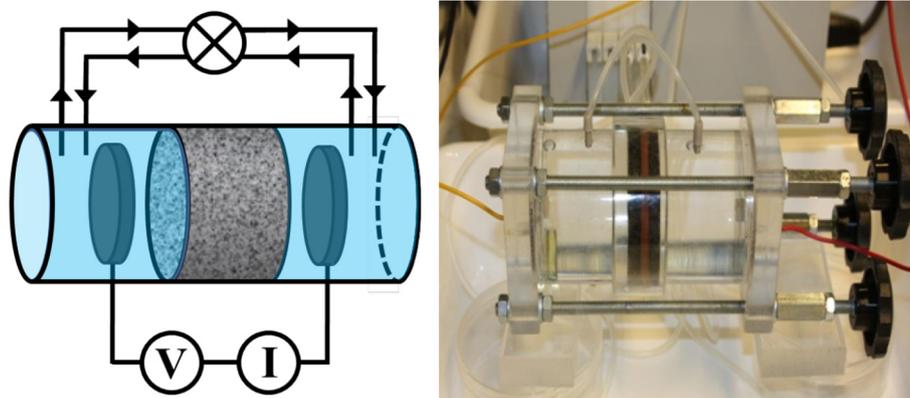
**Fig. 2.** *A schematic diagram of the electromigration equipment (left) that consists a voltage source and meter (V), ammeter (I), peristaltic pump (X), platinum electrodes and drill core sample and a photograph of the electromigration experimental vessel (right) showing the drill core samples in the middle of two chambers.*

assumed that pore space of the rock affects the effective diffusion coefficient and resistivity of the rock similarly. This assumption leads to $F_f$ being equivalent with the pore geometry factor (G) that commonly defined to be a function of porosity and tortuosity. In our experiments there were $Cl^-$ and $Na^+$ ions in the solution and their diffusion coefficients in water at room temperature are $2.0 \times 10^{-9}\,m^2/s$ and $1.3 \times 10^{-9}\,m^2/s$, respectively. Their average value ($1.65 \times 10^{-9}\,m^2/s$) was used when determining the effective diffusion coefficients.

## 3. Results

### 3.1. Porosities, formation factors and effective diffusion coefficients

The porosities, formation factors and effective diffusion coefficients of the drill core samples used in the electromigration sorption experiments are presented in Table 2. The observed porosity values represent the typical values for rock samples taken from the Olkiluoto area (Smellie et al., 2014). However, these values are closer to the low porous end of typical values. There was no correlation found between the determined porosities and rock type that is typical for crystalline rock samples taken from the same site.

The results for $F_f$ and $D_e$ are given as an uncertainty weighted averages over all independent measurements. Here different electric potentials and their uncertainties were taken into account. The

**Table 2**
The average volumetric porosities, formation factors ($F_f$) and effective diffusion coefficients ($D_e$) of rock samples used in the electromigration sorption experiments (a number of core samples permeasurements in parentheses). The values are given as an uncertainty weighted average over all individual experiments and given uncertainties are uncertainties of the weighted average. Uncertainty of individual core samples varied between 20% and 50% for porosity, between 4% and 21% for the formation factor and between 4% and 20y% for the effective diffusion coefficient.

| Rock Type | Sample (number of samples) | Porosity (%) | $F_f \times 10^{-5}$ (−) | $D_e \times 10^{-14}$ ($m^2/s$) |
|---|---|---|---|---|
| Mica gneiss (MGN) | PP219 (6) | 0.26 ± 0.05 | 14 ± 3 | 24 ± 6 |
| | PP309 (6) | 0.07 ± 0.01 | 4 ± 2 | 7 ± 3 |
| | PP131(51) (3) | 0.36 ± 0.02 | n.d. | n.d. |
| | MGN average | 0.23 ± 0.12 | 11 ± 8 | 18 ± 13 |
| Tonalite-granodiorite-granite-gneiss (TGG) | PP175 (7) | 0.07 ± 0.01 | 3 ± 2 | 6 ± 4 |
| | KR56 (3) | 0.19 ± 0.08 | 38 ± 7 | 64 ± 11 |
| | KR43 (2) | 0.22 ± 0.01 | n.d. | n.d. |
| | TGG average | 0.15 ± 0.08 | 13 ± 17 | 22 ± 29 |
| Pegmatitic granite (PGR) | PP131(70) (2) | 0.46 ± 0.06 | n.d. | n.d. |
| | PP249 (3) | 0.19 ± 0.01 | n.d. | n.d. |
| | PGR average | 0.30 ± 0.15 | n.d. | n.d. |

n.d. = not determined.

variations of the results over each drill core and rock type arise from the heterogeneity of the rock and, more importantly, the heterogeneity of the pore structure. Such variations are common in crystalline rock at the studied scale (Sammaljärvi et al., 2017).

The average effective diffusion coefficients of MGN samples were $(24 \pm 6) \times 10^{-14}\,m^2/s$ (PP219) and $(7 \pm 3) \times 10^{-14}\,m^2/s$ (PP309). The difference is relatively small when taking into account the differences in mineral composition, grain size and foliation. It can be concluded that slightly larger grain size (probably lower tortuosity of pore space) and more heterogeneous structure of the PP219 drill core has caused its slightly larger $D_e$ compared with one of PP309 drill core. These values are also in accordance with the porosities (PP219: 0.24 ± 0.04%; PP309: 0.07 ± 0.01%). Typically a sample with higher porosity has a higher $D_e$ than a sample with lower porosity if the pore structure remains similar.

The average effective diffusion coefficients for TGG samples were $(6 \pm 4) \times 10^{-14}\,m^2/s$ (PP175) and $(64 \pm 11) \times 10^{-14}\,m^2/s$ (KR56). The difference is over one order of magnitude and it reflects large differences in mineral composition and in pore structure between these rock samples. Examination of the mineral compositions reveal (see Table 1) that the PP175 samples have much higher content of biotite than the KR56 samples. The pore space of biotite consists of space between the randomly ordered biotite grains and nanometer scale apertures between the biotite lamellae within each grain. The nanometer scale pores have extremely low constrictivity and they tend to decrease the $D_e$ of the rock if biotite content is high. In this case straight conclusion according to porosity (PP175: 0.07 ± 0.01%; KR56: 0.19 ± 0.08%) and $D_e$ cannot be drawn due to the remarkable difference in mineral content and pore structure. However, the porosities happen to be larger for the samples from the drill core KR56 than the ones from the drill core PP175. For all of the samples determined effective diffusion coefficients are within the range of ones determined in earlier studies (Smellie et al., 2014). However, the values are closer to the high diffusivity end of typical values.

### 3.2. Distribution coefficients for intact rock and their up scaling factors

The electromigration sorption experiments were done to determine the distribution coefficients of cesium and strontium for intact rock and to determine the upscaling factors for distribution coefficients from crushed to intact rock. Seven example curves for the concentration of cesium in the solution chambers as a function of time are shown in Fig. 3. These concentration curves represent the rate of sorption: larger change indicates greater sorption and a larger distribution coefficient. The experiments were run until a steady state concentration was reached. Typically, the equilibrium was reached after 2000–7000 h (see Fig. 3). The equilibrium concentration was then used for determining
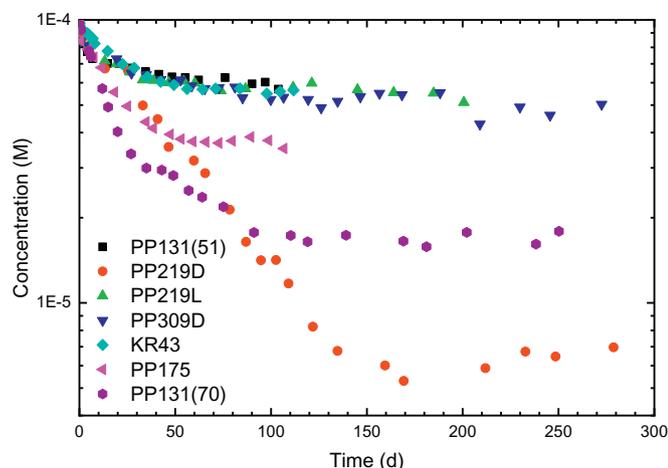
**Fig. 3.** Concentration of cesium as a function of time in seven out twenty-eight electromigration sorption experiments. Initial cesium concentration was $10^{-4}$ M.

the distribution coefficients (see Table 3). It is obvious that porosity, $K_d$ and $F_f$ of the rock affect the shape of the concentration curve and the time when equilibrium is reached. The $K_d$ determines the value where the concentration levels out. Because electric potential is used to transport cesium through the sample, and more importantly closer to the potential sorption sites, the $F_f$ affects the curve part before leveling out. In practice, for samples with high $F_f$ the concentration becomes constant faster than the ones with low $F_f$ (e.g. see curve for PP131(70) in Fig. 3). For samples with a low $F_f$, it takes a long time to achieve the equilibrium concentration since it takes time to reach the sorption sites even with electric potential as driving force.

The distribution coefficients were determined from the steady state concentration using Eq. 1 and the results for all rock samples and averages for studied rock types are given in Table 3. The selection criteria for equilibrium concentration were as follows:

1. If the concentration had leveled, an average of the 2–3 last values was used.
2. If the concentration had an increasing trend at the end of the experiment, the average value of all points after an initial decrease was used
3. If the concentration was still decreasing at the end of the experiment, " < " sign was used to indicate that the steady state value is smaller than the presented one. This means that steady state value for distribution coefficients (crushed and intact) are greater than the presented ones. In this case the upscaling factor is given as most probable value and is indicated with "~" sing.

The distribution coefficients of cesium for crushed rock were taken from curves presenting the distribution coefficients as a function of cesium concentration (Lehto et al., 2018) at the same cesium concentration as was the equilibrium concentration in the electromigration sorption experiment with the same rock sample. For the samples not studied by Lehto et al. (2018) (PP131(51), KR43, PP131(70) and PP249) the distribution coefficients were determined by separate experiments with equilibrium concentration of about 50 μM that was a typical value for equilibrium concentration is these experiments.

The distribution coefficients of cesium for crushed rock are from 1.1 to 60 times greater than the ones of intact rock (see Table 3). In general, the batch sorption experiments exaggerate the distribution coefficient of intact rock considerably and the average upscaling factors of 7 ± 4, 3 ± 1 and 33 ± 30 were determined for MGN, TGG and PGR samples, respectively. The variances between different rock types, however, are

**Table 3**

The distribution coefficients ($K_d$) of cesium for intact Olkiluoto rocks from the electromigration sorption experiments and ones for crushed rocks at the same equilibrium concentration (Lehto et al., 2018). The upscaling factors ($F_U$) are given as a ratio of distribution coefficients of crushed and intact rocs. The average values are given as uncertainty weighted averages and initial cesium concentration was $10^{-4}$ M.

| Sample | Rock type | Intact rock $K_d$ (m³/kg) $1 \times 10^{-3}$ | Equilibrium Cs concentration (μM) | Crushed rock $K_d$ (m³/kg) $1 \times 10^{-3}$ | $F_U$ (−) |
|---|---|---|---|---|---|
| PP131(51)_1 | MGN | 2.8 ± 0.5 | 53 ± 5 | 25 ± 8 | 9 ± 3 |
| PP131(51)_2 | | 11.4 ± 0.5 | 20 ± 1 | 36 ± 9 | 3.2 ± 0.8 |
| PP131(51)_3 | | 2.3 ± 0.2 | 59 ± 4 | 24 ± 6 | 10 ± 3 |
| PP219A | | 27 ± 2 | 11 ± 1 | 46 ± 7 | 1.7 ± 0.3 |
| PP219D | | 50 ± 6 | 6.2 ± 0.3 | 57 ± 9 | 1.1 ± 0.3 |
| PP219H | | 1.8 ± 0.5 | 67 ± 13 | 22 ± 5 | 12 ± 5 |
| PP219L | | 2.5 ± 0.4 | 58 ± 6 | 24 ± 4 | 9 ± 2 |
| PP309A | | > 4.0 | < 48 | > 16.3 | ~4.1 |
| PP309D | | 3.4 ± 0.3 | 49 ± 3 | 16.2 ± 1.3 | 4.8 ± 0.6 |
| PP309H | | 1.2 ± 0.3 | 75 ± 13 | 14 ± 2 | 11.8 ± 4 |
| PP309L | | 2.6 ± 0.1 | 57 ± 3 | 15.5 ± 1.1 | 6.0 ± 0.5 |
| PP309C | | 1.8 ± 0.1 | 64 ± 9 | 15 ± 2 | 8.3 ± 1.1 |
| PP309E | | 3.5 ± 0.1 | 44 ± 4 | 17 ± 2 | 4.8 ± 0.5 |
| **MGN average** | | **2.7 ± 0.6** | | **17 ± 3** | **7 ± 4** |
| KR43_1 | TGG | 2.6 ± 0.2 | 42 ± 2 | 12.1 ± 1.1 | 4.7 ± 0.6 |
| KR43_2 | | 3.5 ± 0.3 | 52 ± 3 | 11.4 ± 1.0 | 3.3 ± 0.4 |
| KR43_4 | | 4.9 ± 0.1 | 51 ± 3 | 11.6 ± 1.0 | 2.4 ± 0.3 |
| PP175A | | 4.7 ± 0.3 | 64 ± 4 | 12.9 ± 1.0 | 2.7 ± 0.3 |
| PP175D | | 5.9 ± 0.3 | 68 ± 4 | 13.4 ± 1.0 | 2.3 ± 0.3 |
| PP175V | | 4.1 ± 0.1 | 61 ± 3 | 12.6 ± 0.9 | 3.1 ± 0.8 |
| KR56Q | | > 0.7 | < 81 | > 2.1 | ~3.1 |
| KR56O | | > 1.6 | < 64 | > 2.2 | ~1.4 |
| **TGG average** | | **4 ± 2** | | **10 ± 5** | **3 ± 1** |
| PP249_1 | PGR | 0.22 ± 0.05 | 90 ± 2 | 8.1 ± 0.7 | 37 ± 9 |
| PP249_2 | | 0.13 ± 0.02 | 94 ± 1 | 7.8 ± 0.7 | 60 ± 10 |
| PP249_3 | | 0.12 ± 0.05 | 95 ± 2 | 7.7 ± 0.7 | 60 ± 30 |
| PP131(70)_11 | | 17.7 ± 1.3 | 17 ± 1 | 27 ± 3 | 1.5 ± 0.2 |
| PP131(70)_12 | | 26.2 ± 1.1 | 11 ± 1 | 32 ± 4 | 1.2 ± 0.2 |
| **PGR average** | | **1 ± 11** | | **30 ± 11** | **33 ± 30** |

not very similar. For rock samples with a high biotite content the variation of the upscaling factors are rather similar whereas for PGR samples higher variation was observed. For the MGN samples the upscaling factors vary from 1.1 to 12, for the TGG samples they vary from 1.4 to 4.7, and for PGR samples they vary from 1.2 to 60. In general, the variations in the upscaling factors are rather high which might make it difficult to convert a distribution coefficient of single batch sorption to one for intact rock. For MGN and TGG samples the variation can be explained by heterogeneity in the porespace and mineral content of the rock samples that can be seen in Fig. 1. Furthermore, for samples of each drill core there are both low and high upscaling factors determined. Previously Kuva et al. (2018) have shown the effect of mineral heterogeneity on the transport of cesium in crystalline rock samples from Olkiluoto. For PGR samples the low upscaling factors were determined for samples of PP131(70) and the high upscaling factors for the ones from PP249. The same applies also for distribution coefficients determined for both intact and crushed rock. The PGR samples contain a few percent of biotite and variation in its content cannot explain this. However, it is plausible that the samples of the different drill core have undergone different alteration processes. Due to seritization and muscovization of plagioclase more reactive mineral grains and more surface area is created. Effect of this can be seen as a higher distribution coefficient of cesium for the samples of the drill core PP131 than the ones of the drill core PP249. When less altered drill core PP249 is crushed respectively more surface area is created and thus the upscaling factor becomes greater for less altered samples than for more altered ones. Lehto et al. (2018) observed that crushing does not only create more surface on the outer surfaces of the grains but also the inner surface due to mechanical stress. Proportion of inner and outer surfaces varied considerably from sample to another and grain size affected significantly proportion. It can be concluded that alteration state of the sample can affect considerably the distribution coefficient and the upscaling factor and thus a number of measurement using samples with different alteration states should be used in order to get a representative result for the average upscaling factor.

There was no clear correlation found between effective diffusion coefficient and distribution coefficient. It seems that pore structure of the rock affects more the effective diffusion coefficient, whereas the distribution coefficient and upscaling factor are more affected by the mineral content and alteration state.

The electromigration sorption experiments were done for strontium with drill cores PP219 (MGN) and PP175 (TGG). Example curves for the decrease of strontium concentration in the solution phase as a function of time are shown in Fig. 4. As in the cesium experiments, these
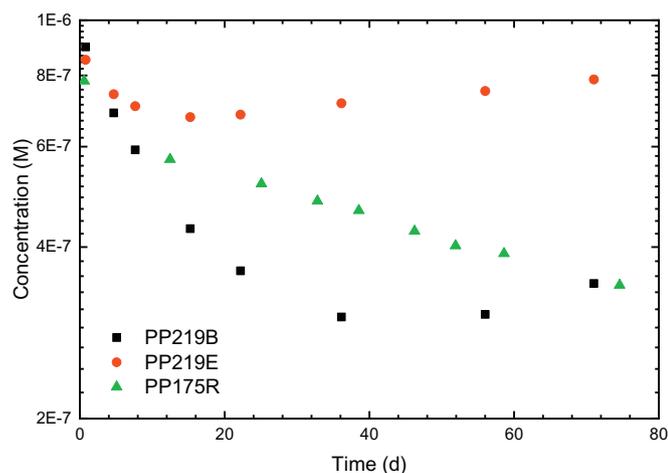
**Table 4**
The distribution coefficients of strontium ($K_d$) for intact Olkiluoto rocks from the electromigration sorption experiments and corresponding values for crushed rocks at the same equilibrium concentration. The upscaling factors ($F_U$) are given as a ratio of the distribution coefficients of crushed and intact rocs. The average values are given as uncertainty weighted averages and initial strontium concentration was $10^{-6}$ M.

| Sample | Rock type | Intact rock $K_d$ (m³/kg) $1 \times 10^{-3}$ | Equilibrium Sr concentration (μM) | Crushed rock $K_d$ (m³/kg) $1 \times 10^{-3}$ | $F_U$ (−) |
|---|---|---|---|---|---|
| PP219B | MGN | 7.4 ± 0.8 | 0.32 ± 0.02 | 17.6 ± 0.6 | 2.4 ± 0.3 |
| PP219E | | 1.4 ± 0.3 | 0.72 ± 0.1 | 17.3 ± 0.6 | 12 ± 3 |
| **MGN average** | | **4.4 ± 3.0** | | **17.4 ± 0.2** | **4 ± 3** |
| PP175A | TGG | > 13.3 | < 0.14 | 40 ± 2 | < 3.0 |
| PP175E | | > 5.7 | < 0.25 | 40 ± 2 | < 7.0 |
| PP175R | | > 6.3 | < 0.34 | 40 ± 2 | < 6.4 |
| PP175U | | > 3.8 | < 0.42 | 40 ± 2 | < 10.5 |
| **TGG average** | | **7 ± 3** | | **40 ± 2** | **7 ± 2** |

experiments were run until an equilibrium concentration was reached (typically 300–1400 h). The equilibrium concentration was then used for determining the distribution coefficients (see Table 4). The concentration of strontium was still decreasing at the end of the experiments with PP175 samples and thus the distribution coefficients are given as lower limits in Table 4. For drill core PP219 (MGN), the concentration starts to increase slightly after 20–60 days which is plausibly caused by small changes in water chemistry due to water-rock interaction. The effect of the concentration decrease has been, however, taken into account as higher uncertainty for equilibrium concentration. For strontium, the equilibrium concentration did not affect considerably the distribution coefficient for crushed rock at the studied concentration range (Lehto et al., 2018) and thus the maximum values for the upscaling factors of PP175 samples are given. The shape of the concentration curves and the value for leveling out were otherwise interpreted in the same way as for the cesium curves. The concentration curves for MGN samples leveled out faster than the ones for TGG samples which is caused by systematic difference in the measured formation factors and effective diffusion coefficients. The distribution coefficients of strontium for crushed rock have been measured by Lehto et al. (2018).

The values of the upscaling factors for strontium did not differ considerably from those of cesium with MGN and TGG (no experiments were done with PGR). Also for strontium the batch sorption experiments exaggerate the distribution coefficient of intact rock considerably and the average upscaling factors of 4 ± 3 and 7 ± 2 were determined for MGN and TGG, respectively (see Table 3). For the MGN samples the upscaling factors vary from 2.4 to 12, for the TGG samples they vary from 3 to 10.5. As in the measurements using cesium the variation in mineral content and heterogeneity can explain the variation of results within both rock types. Furthermore, there was no correlation found between the upscaling factor and effective diffusion coefficient. In general, there is no significant difference between the results of cesium and strontium and thus it can be concluded that variation in the mineral content and properties of the rock affect more the results than radionuclide in question. Here we have used cesium and strontium that both are sorbed on the mineral surfaces by ion exchange.

## 4. Discussion

The determined porosities and diffusion coefficients were within the range of ones determined in earlier studies. However, the values for effective diffusion coefficients were closer to the high diffusivity end of typical values while the porosities were closer to the low porosity end. These findings are in contradiction as, in general, effective diffusion coefficient increases with increasing porosity. Observed effect is likely



**Fig. 4.** Concentration of strontium in three out of six electromigration sorption experiments with PP219 (MGN) and PP175 (TGG) as a function of time. Initial strontium concentration was $10^{-6}$ M.

arising from the slight overestimation of the effective diffusion coefficients by the electrical formation factor measurements. Löfgren (2015) compared effective diffusion coefficients determined by through diffusion measurements and electrical formation factor measurements from earlier studies and found that the electrical methods tend to overestimate the effective diffusion coefficient by a factor of 1.2 to 2.4 potentially due to presence of electrically conductive mineral grains. The variation in the over estimation is fairly high and is clearly dependent on the content of the electrically conductive mineral grains within the transport routes. On the other hand, the content of these minerals must correlate with the rock type. In order to improve knowledge between overestimation and rock type further studies could be performed.

It was shown that the distribution coefficients for intact rock are considerably lower than the ones determined for crushed rock. However, the variations of the upscaling factors were found to be rather high which reduces their applicability when converting results of batch sorption experiments for intact rock. The upscaling factors give further insight which kind of values should be used when estimating the distribution coefficient of intact rock based on results for crushed rock as most of the distribution coefficients used in current safety assessment are determined by batch sorption experiments. However, in future studies it would be beneficial to use the electromigration sorption experiments for determining distribution coefficients in order to increase the confidence of the results. Currently the batch sorption experiments are needed for studying the sorption of redox sensitive radionuclides. In theory, it might be possible to study the sorption and diffusion of the redox sensitive radionuclides. This, however, would require further development of the measurement setup and experimental techniques due to, e.g., the effect of electrical voltage on the oxidation state.

## 5. Conclusions

The main aim of this work was to determine the distribution coefficients of intact rock and to produce the upscaling factors of distribution coefficients determined by batch sorption experiments to those of intact rock. To this end, the electromigration sorption experiments were performed here for intact samples and the upscaling factors were determined using the distribution coefficients determined for crushed rock samples by Lehto et al. (2018).

It was shown that the distribution coefficients of cesium and strontium for intact rock are considerably lower than the ones determined for crushed rock and thus it can be concluded that the electromigration sorption experiments offer a more realistic approach to determine the distribution coefficients of radionuclides for intact rock. The average upscaling factor for different rock types varied from 3 to 33 that shows large variation within rock types. These factors can be used to convert the distribution coefficients of cesium and strontium for crushed rock to ones for intact rock. It was concluded that heterogeneity of the rock, alteration state and mineral content affect the distribution coefficients and further the upscaling factors. The upscaling factors for cesium and strontium are very similar and the properties of the rock affect more the results than the radionuclide in question. In general, the sorption parameters determined here offer ways for a less conservative approach (with respect to the current approach) for the safety assessment of spent nuclear fuel repositories. Furthermore, the methods used here can be applied for other safety relevant anionic and cationic radionuclides.

The determined effective diffusion coefficients and porosities were in agreement with previously determined values for samples of Olkiluoto. The methods applied offer fast and reliable ways to measure these parameters before the electromigration sorption experiments without destroying the samples. In the end, all three parameters of bedrock used in the safety assessment of the spent nuclear fuel repositories were determined here for exactly the same samples. The values can be directly applied in the safety assessment and they can be used to increase its confidence and decrease the conservativeness of the values used current in safety assessment.

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