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

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ABSTRACT

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 $(0.12–26.2) \times 10^{-3}\,m^3/kg$ and $(1.4–13.3) \times 10^{-3}\,m^3/kg$, respectively, whereas recent results for crushed rock varied between $(2–57) \times 10^{-3}\,m^3/kg$ and $(17–40) \times 10^{-3}\,m^3/kg$, 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° (PP309) and -89.5° (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