



The sorption and diffusion of ^{133}Ba in crushed and intact granitic rocks from the Olkiluoto and Grimsel in-situ test sites

Eveliina Muuri^{a,*}, Minja Matara-aho^a, Eini Puhakka^a, Jussi Ikonen^a, Andrew Martin^b, Lasse Koskinen^c, Marja Siitari-Kauppi^a

^a Department of Chemistry, University of Helsinki, P.O. Box 55, 00014, Helsinki, Finland

^b Nagra (National Cooperative for the Disposal of Radioactive Waste), Wettingen, Switzerland

^c Posiva Oy, Finland

ARTICLE INFO

Keywords:

Sorption

Diffusion

Nuclear waste

Crystalline rock

Barium

ABSTRACT

The distribution coefficients of barium on Olkiluoto pegmatitic granite and veined gneiss, Grimsel granodiorite and their main minerals (quartz, plagioclase, potassium feldspar and biotite) were obtained by batch sorption experiments carried out as a function of the concentration of barium. The distribution coefficients on biotite and veined gneiss were modelled with the PHREEQC computing program. In addition, the diffusion of barium into rock cubes was also studied both experimentally and computationally and the rock cubes from the diffusion experiments were studied with autoradiography and scanning electron microscopy. The results showed that the distribution coefficients of barium were largest on biotite and the sorption as a function of barium concentration on all the minerals followed a similar trend. The distribution coefficients of barium on veined gneiss, pegmatitic granite and granodiorite followed the distribution coefficient trend of their main minerals and the distribution coefficients were largest on granodiorite due to the low salinity of the groundwater simulant. The distribution coefficients of barium on veined gneiss were of the same magnitude as on granodiorite because of the high biotite content of veined gneiss and those on pegmatitic granite were a magnitude smaller. It was also discovered that the distribution coefficients in saline water were considerably smaller than the results obtained in low salinity water, which suggests that competing ions play a significant role in the sorption of barium. Finally, the concentration decrease of barium in the solution in the diffusion experiments was largest in granodiorite which can be explained with both the porous structure of all the minerals of granodiorite leading to high accessible surface area and with the sorption properties of barium. It was discovered with autoradiography that the barium was mainly sorbed on the dark minerals of the rocks, but, additionally, barium sorption on plagioclase was also concluded to be significant. In addition, the sorbed barium could be seen with scanning electron microscopy on the biotite and calcite veins in the fissures of the rock in granodiorite and veined gneiss.

1. Introduction

Spent nuclear fuel in Finland will be disposed of in the crystalline granitic bedrock 400 m below surface at the Olkiluoto site in a repository system that is based on a multiple barrier system consisting of copper-iron canisters isolated by bentonite and the bedrock (Miller and Marcos, 2007). The bedrock in the Olkiluoto site is considered suitable for the facility due to its stable tectonic setting, good quality, existing reducing conditions and low groundwater flow at the repository system depth (Posiva Oy, 2012). However, the processes affecting the migration of the radionuclides from the nuclear fuel need to be taken into account when assessing the overall safety of the repository. It is therefore very important to study the sorption and diffusion properties

of different radionuclides through laboratory and in-situ field work in order to assess the physical and chemical processes affecting the migration of radionuclides in the different release barriers of the repository including the bedrock.

The radionuclides occurring in the spent nuclear fuel have been divided into five priority classes in the Finnish safety calculations according to their relevance for the safety assessment; top priority, high priority (I), high priority (II), high priority (III) and low priority (Posiva Oy, 2013). The first class is the top priority class containing the non-sorbing radionuclides which are expected to dominate the radioactive dose (^{14}C , ^{36}Cl , ^{129}I). ^{226}Ra is commonly placed in the low priority class but it needs to be taken into account in some calculation cases in the biosphere assessment as it is enriched in the system as the daughter

* Corresponding author.

E-mail address: eveliina.muuri@helsinki.fi (E. Muuri).

nuclide in the uranium series (Haavisto, 2014; Posiva Oy, 2008). In contrast with the Finnish safety calculations, it has been noted in some scenarios in the Swedish safety calculations that one of the largest long-term radiological risks to humans over a certain time span will be caused by radium (Svensk Kärnbränslehantering AB, 2006). Radium occurs in the oxidation state + II and its compounds are relatively soluble which makes radium mobile should a leakage occur in the repository (Lehto and Hou, 2011). In addition, the activity of radium in the spent nuclear fuel will increase reaching its maximum after approximately 300,000 years (Hedström, 2013). However, the investigation of ^{226}Ra is complicated because it is an alpha emitter in the uranium series and chemical separation is needed for the alpha spectrometry. In addition, the strongest gamma transition of ^{226}Ra is the same and has similar intensity as that of a peak of ^{235}U (Lehto and Hou, 2011). It is therefore common to use the gamma emitting ^{133}Ba as an analogue for ^{226}Ra . Barium and radium are both alkali earth metals with very similar chemical properties and, as a consequence, ^{133}Ba is one of the nuclides studied in the in-situ experiments (Widestrand et al., 2004; Voutilainen et al., 2014).

The sorption and diffusion of barium have been studied in laboratory and in-situ conditions (Möri et al., 2003a, b; Hakanen et al., 2014). However, long-term in-situ experiments are time-consuming and costly due to which only few of them have been carried out. In 2009 a long-term diffusion project was started in the Grimsel Test Site in Switzerland to evaluate the diffusion and sorption properties of radionuclides in the in-situ conditions (Jokelainen et al., 2013; Soler et al., 2015; Ikonen et al., 2016a, 2016b). In addition, several in-situ diffusion tests are currently ongoing in the Olkiluoto site in Finland (Voutilainen et al., 2014). All these experiments need supporting laboratory studies as it is highly important to compare the scarce in-situ results with the laboratory experiments to better assess their relevancy.

In this study, the sorption and diffusion of barium were investigated with laboratory experiments and with computer modelling to support the results from the in-situ experiments. The laboratory experiments were conducted in conditions that were resembling the conditions in the Grimsel and Olkiluoto in-situ test sites. The sorption of barium was studied with batch sorption experiments in a broad concentration range (10^{-9} – 10^{-3} M) in Grimsel granodiorite, Olkiluoto pegmatitic granite and veined gneiss, and their main minerals; quartz, plagioclase, potassium feldspar and biotite. The diffusion of barium was studied in rock cubes of granodiorite, pegmatitic granite and veined gneiss as a function of time. Groundwater simulants resembling the fracture waters in the Grimsel and Olkiluoto sites were used in the batch sorption experiments and in the diffusion experiments. The sorption results were modelled with the PHREEQC computer program after justifying the sorption model with molecular modelling based on density functional theory (DFT). The COMSOL Multiphysics software was employed in the modelling of the diffusion results. The aim of the diffusion modelling was to better describe the retention of barium in intact crystalline rock in the conditions of the geological repository.

2. Materials and methods

2.1. The geology and mineralogy of the Grimsel and Olkiluoto site

The Grimsel Test Site is located in central Switzerland at an altitude of 1730 m in the granitic rock of the Aare Massif which is consisted of a metasedimentary envelope that was intruded by Hercynian granitoids (320–280 Ma) (Tachi et al., 2015). All the rocks in the area have been affected by the Alpine greenschist metamorphism and deformation and the still ongoing post-metamorphic regional uplift (Möri et al., 2003a). The bedrock in the Grimsel test site area is composed of granodiorite (Hoehn et al., 1998) and Aare granite and the long-term diffusion tests have been conducted in the areas consisted of granodiorite (Hu and Möri, 2008; Möri et al., 2003b). Grimsel granodiorite is homogeneous, medium grained and slightly preferentially-oriented with brittle

Table 1

The average mineral compositions of veined gneiss, pegmatitic granite and granodiorite in volume percentage by point counting method (500 points/thin section), where + is optically observed. (Ikonen et al., 2015; Jokelainen et al., 2013).

Mineral	Veined gneiss	Pegmatitic granite	Granodiorite
Quartz	30.2	36.0	32.8
Plagioclase	19.0	44.8	36.5
Potassium feldspar	4.4	12.8	34.4
Biotite	35.2	+	6.4
Muscovite	2.2	5.0	2.1
Chlorite	–	+	0.3
Cordierite	2.2	–	–
Garnet	–	1.4	–
Sillimanite	6.6	–	–
Epidote	+	+	1.1
Apatite	+	–	–
Opaque	0.2	+	0.1
Titanite	–	–	0.3
Amphibole	–	–	3.2

structural features of cataclastic fault breccias and discrete faults (Möri et al., 2003b). The main minerals of granodiorite are quartz, plagioclase, potassium feldspar and biotite (Table 1). Other minerals, which do not exceed 5% in volume, are green amphibole (hornblende), muscovite, epidote, titanite and opaque minerals (Jokelainen et al., 2013).

The Olkiluoto site, on the other hand, is an island located on the coast of south-western Finland where the repository system will be built in the depth of 400 m below the surface. The site is situated in the part of the Fennoscandian shield where the postglacial land uplift is moderate, about 6 mm annually. The latest glaciation in southern Finland lasted over 50,000 years and the ice sheet retreated from the Olkiluoto site about 10,000 years ago (Pitkänen et al., 1996). The bedrock in the area is of heterogeneous Archaean crystalline rock. The degree of heterogeneity and foliation change rapidly in the bedrock in Olkiluoto area where the main rock type in the depth of the deposition facility is veined gneiss (43%) with shorter sections of pegmatitic granite (20%) (Aaltonen et al., 2016). Pegmatitic granite can be found in the host rock as coarse-grained irregular masses whereas veined gneiss shows a high level of deformation with powerful foliation. The main minerals of veined gneiss are quartz, plagioclase, biotite and potassium feldspar and the main minerals of pegmatitic granite are quartz, plagioclase and potassium feldspar (Table 1) (Posiva Oy, 2008; Kärki and Paulamäki, 2006; Ikonen et al., 2015).

2.2. Groundwater simulants

The groundwater in the Grimsel Test Site is alkaline and weakly saline with low ionic strength and few competing ions for barium (Mäder et al., 2006). The chemical composition of the groundwater simulant used in the experiments (Table 2) was prepared based on the

Table 2

The chemical composition of the Grimsel and Olkiluoto groundwater simulants used in the experiments (Mäder et al., 2006; Voutilainen et al., 2014).

Component	Molality	
	Grimsel	Olkiluoto
pH	9.7	6.9
Na^+	$6.9 \cdot 10^{-4}$	$1.2 \cdot 10^{-1}$
K^+	$5.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-4}$
Ca^{2+}	$1.4 \cdot 10^{-4}$	$1.3 \cdot 10^{-2}$
Mg^{2+}	$6.2 \cdot 10^{-7}$	$1.4 \cdot 10^{-3}$
HCO_3^-	$4.5 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
Cl^-	$1.6 \cdot 10^{-4}$	$1.4 \cdot 10^{-1}$
SO_4^{2-}	$6.1 \cdot 10^{-5}$	$3.1 \cdot 10^{-6}$
Br^-	$3.8 \cdot 10^{-7}$	$4.1 \cdot 10^{-4}$
F^-	$3.6 \cdot 10^{-4}$	$7.9 \cdot 10^{-5}$

Download English Version:

<https://daneshyari.com/en/article/8863200>

Download Persian Version:

<https://daneshyari.com/article/8863200>

[Daneshyari.com](https://daneshyari.com)